CHEMICAL FXAMINATION
OF
SEED AND SEED-COAT FATS OF SOME OF THE MEMBERS OF THE FAMILIES UMBELLIFERAE AND LEGUMINOSAE.

(Hypohalogenation of the isomeric pair of 6:7-octadeeenoic acids).

THESIS
SUBMITTED FOR THE DEGREE
OF
DOCTOR OF PHILOSOPHY IN CHEMISTRY
TO
THE ALIGARH MUSLIM UNIVERSITY
ALIGARH

1960. MOHD. SALEEM SIDDIQUI

A B S T R A C T

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RESUMÉ

The work described in this thesis leads to the following conclusions:

1. The hypochlorination of petroselinic acid or hydrohalogenation of petroselinic acid epoxide gives the identical mixtures of 6(7):7(6)-chlorohydroxystearic acids m.p.59-60°.

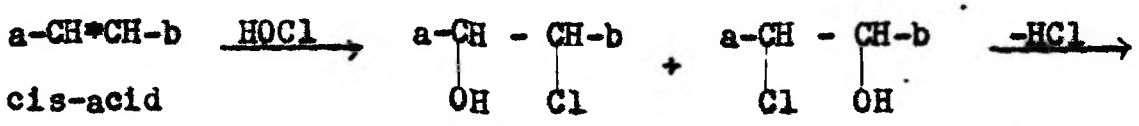
2. The formation of the identical chlorohydrins from two different routes leads to suggest that inversion in configuration occurs during the opening of the epoxide ring by hydrohalogenation.

3. 6(7):7(6)-Chlorohydroxystearic acids (obtained by either of the two methods mentioned above) on dehydrohalogenation give the same cis-6:7-epoxystearic acid, m.p.59-60°.

4. The fact that the epoxy acid formed in the above case is identical with the original one leads to the conclusion that closing of the epoxide ring by dehydrohalogenation is accompanied by inversion in configuration.

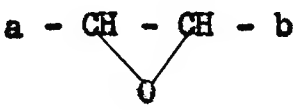
5. trans-Petroselaidic acid when subjected to hypochlorination or the direct hydrohalogenation of its epoxide yields the same mixtures of 6(7):7(6)-chlorohydroxystearic acids m.p.55-56°. These chlorohydrins behave in an analogous manner with the ones obtained from petroselinic acid or

its epoxide. The results of the hypochlorination of isomeric 6:7-octadecenoic acids and their epoxides are given below:

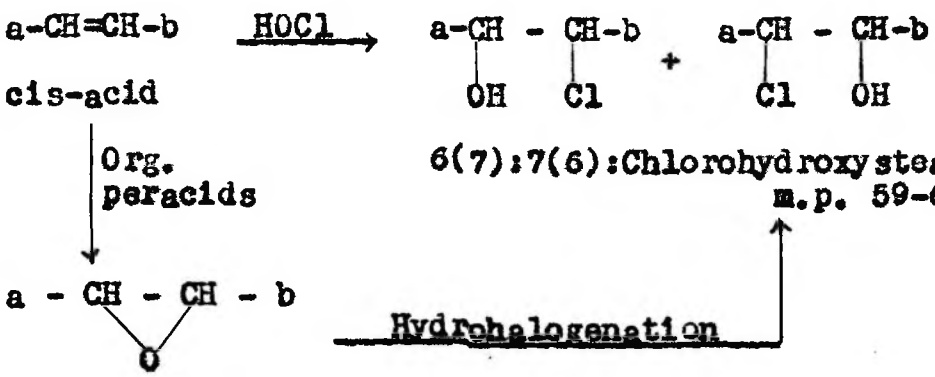


cis-acid

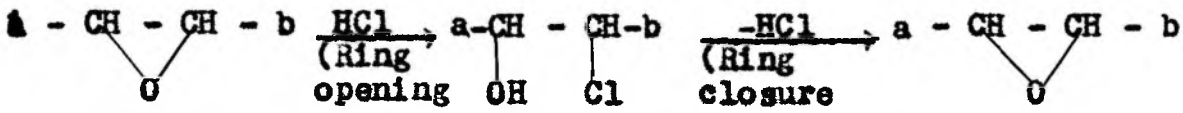
6(7):7(6)-Chlorohydroxystearic acids m.p. 59-60°



cis-epoxy acid

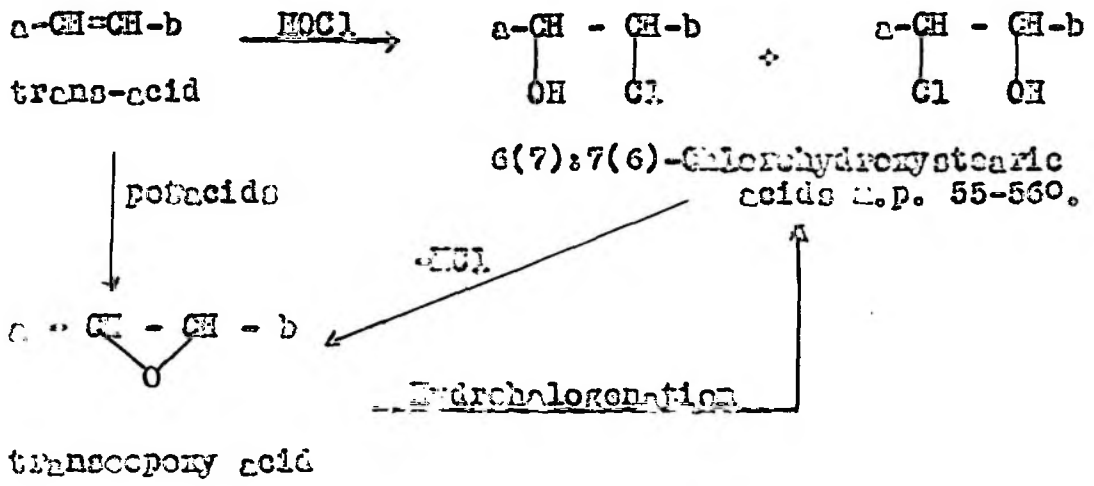


cis-epoxide



cis-epoxy acid

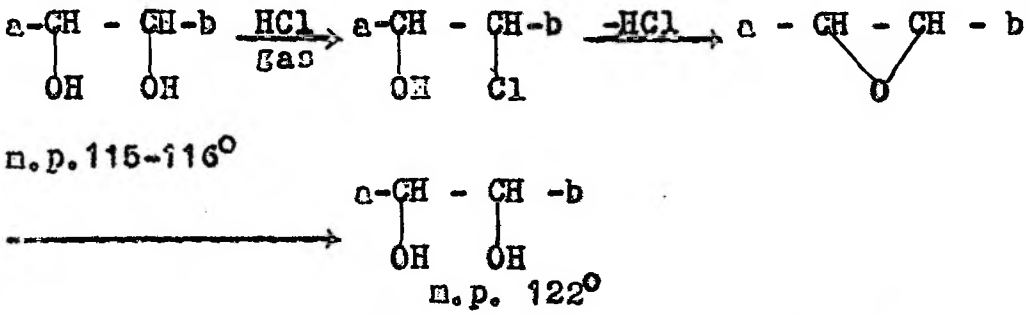
cis-epoxy acid

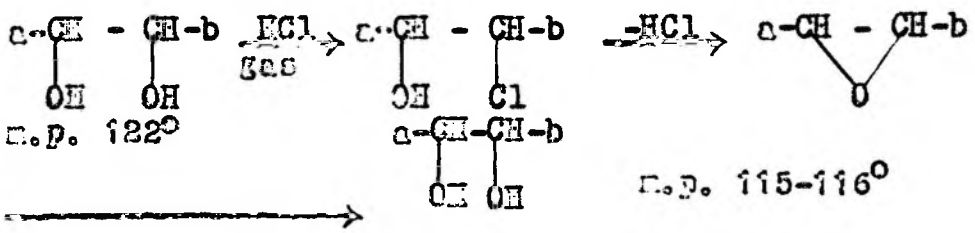


6. The interconversion of erythro-6:7-dihydroxystearic acid m.p. 122° and its stereo-isomer m.p. 115-116° has been successfully carried out through the hydrochlorination and subsequent dehydrochlorination followed by hydrolysis.

7. The results of these interconversions lead to the conclusion that the replacement of one of the hydroxyl groups by a chlorine atom is accompanied by inversion in configuration.

The results are summarised below:

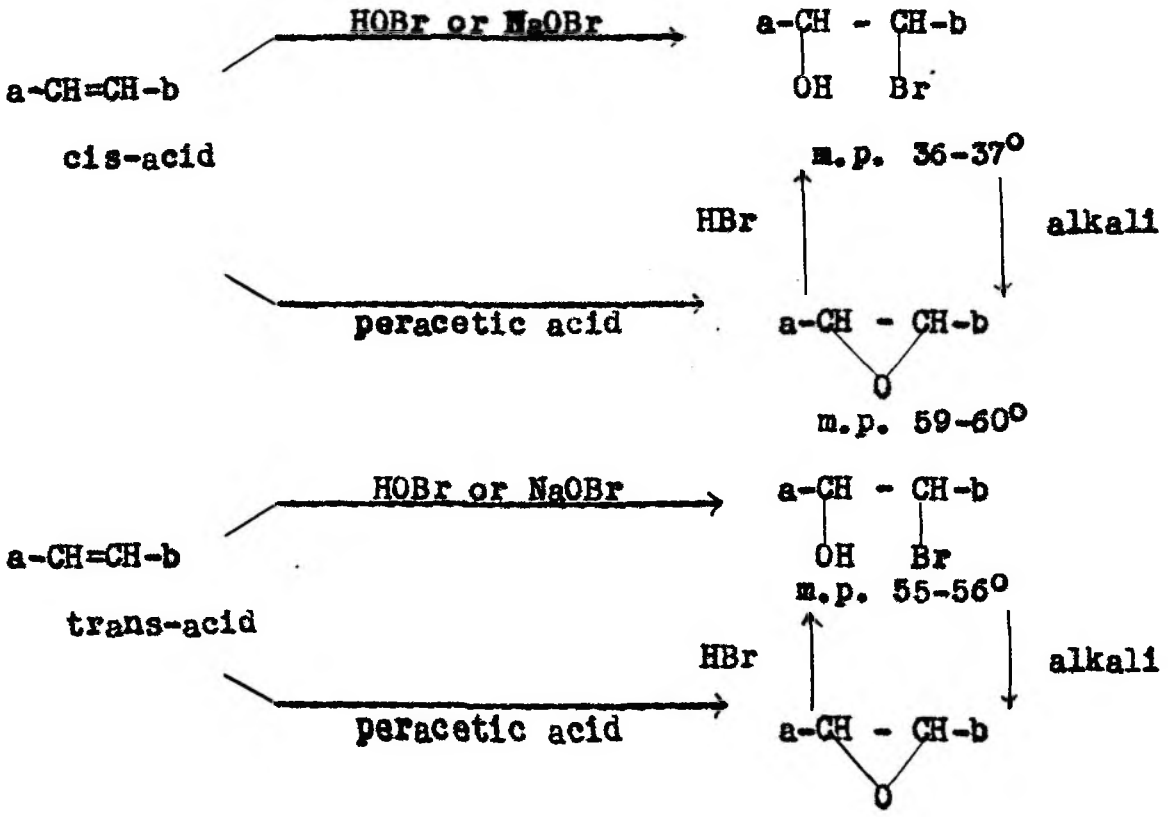




(8) The hypobromination of petroselinic acid or hydrobromination of its epoxide gives the same 6(7):7(6)-bromohydroxystearic acids m.p. 36-37°. These bromohydrins reproduce the original ∝ epoxy acid on dehydrohalogenation.

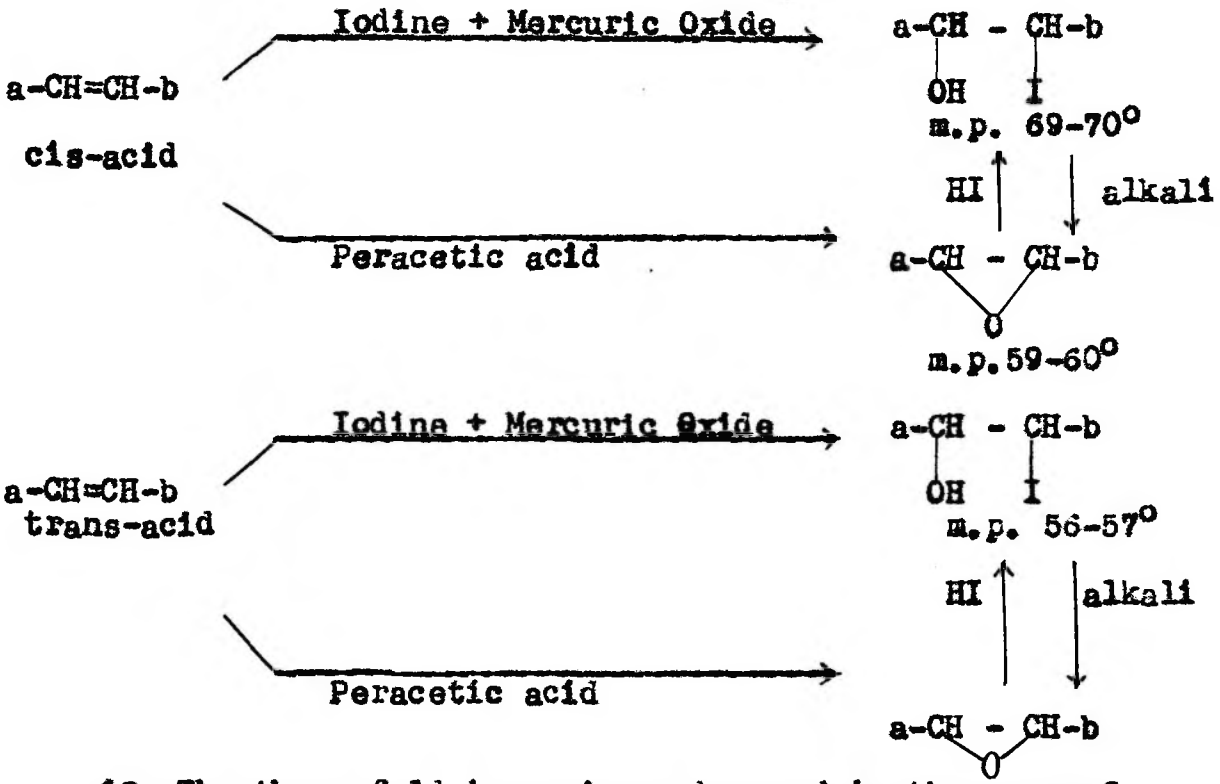
(9) trans-Petroselaidic acid or its epoxide on a similar treatment as mentioned above yield a mixture of 6(7):7(6)-bromohydroxystearic acids m.p. 55-56°. The origina epoxy acid was reproduced when these bromohydrins are dehydro halogenated.

The results of hypobromination are summarised below:



10. Petroselinic acid on treatment with Iodine in presence of mercuric oxide or petroselinic acid epoxide on treatment with hydroiodic acid give the identical mixture of 6(7):7(6)-iodohydroxystearic acids m.p.69-70°. These iodohydrins on treatment with alkali give the original epoxy acid.

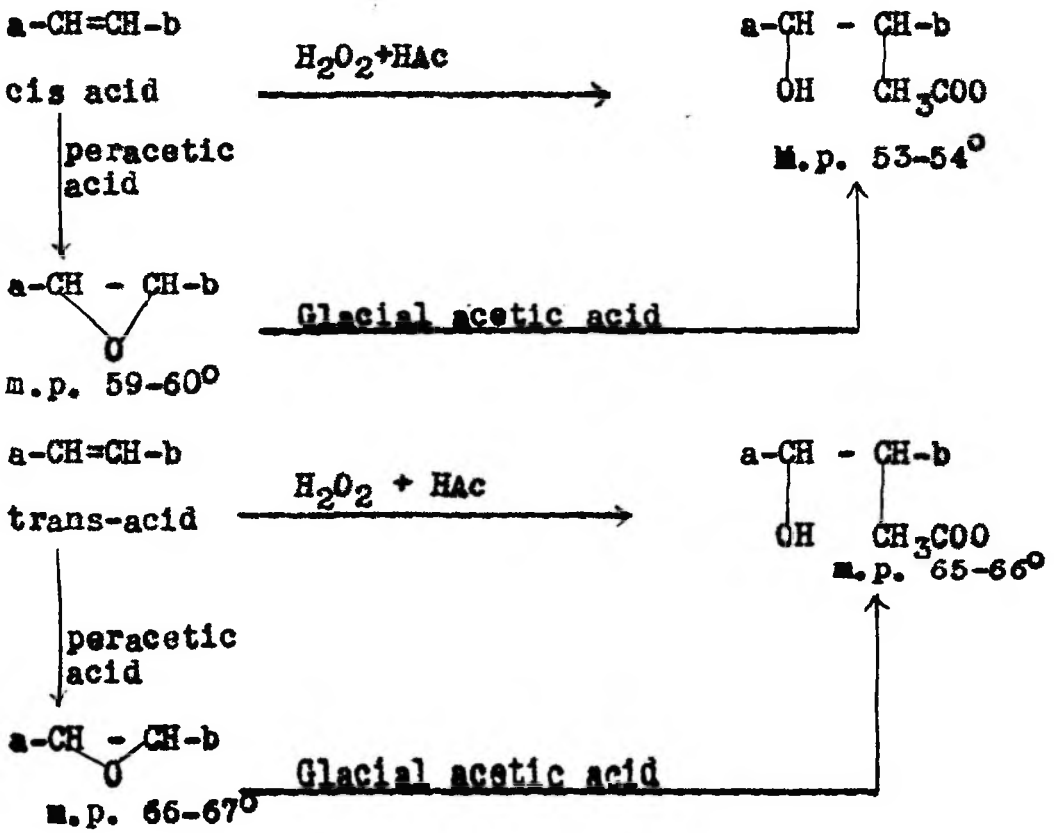
11. Petroselaidic acid or its epoxide on analogous treatments yield 6(7):7(6)-iodohydroxystearic acids m.p.56-57° which on dehydrohalogenation regenerate the original epoxide.



12. The three fold inversions observed in the case of chlorohydrins is confirmed by the analogous behaviour of bromo- and iodo-hydrins.

13. The treatment of petroselinic and petroselaidic acids in glacial acetic acid with hydrogen peroxide yield 6989:7(6)-hydroxyacetoxystearic acids m.p. 53-54°. and m.p. 65-66° respectively. These mono-acetyl derivatives have also been obtained by the action of glacial acetic acid on petroselinic and petroselaidic acid epoxides respectively

14. The formation of hydroxyacetoxystearic acids from the epoxides lead to suggest that these are the intermediates in the coversion of the epoxides to the corresponding dihydroxystearic acids.



15. The fatty acid compositions of the following seed-fats have been determined.

1. Seseli indicum	Family	Umbelliferae
2. Anethum trifoliatum	"	"
3. Albizzia odoratissima	"	Leguminosae
4. Albizzia procera	"	"
5. Leucaena glauca	"	"
6. Haloptela integrifolia	"	Urticaceae

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CONTENTS

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The work described in this thesis was carried out under the supervision of Prof. M.O.Farooq. The author gratefully acknowledges the guidance and encouragement he received from him in carrying out this work.

I N T R O D U C T I O N

The main building materials of all living organisms are the three most important classes of organic compounds, the proteins, the carbohydrates, and the fats. All vital processes are directly linked with the elaboration or degradation of these substances. These complex compounds are synthesised in nature from simple molecules, giving rise to a great variety and abundance of these compounds. The proteins are built up of amino-acids, the carbohydrates are made up of monosaccharides while the fats are esters of higher fatty acids. There is an essential difference in the skeleton of the proteins and the carbohydrates on the one hand and the fats on the other. The proteins and the carbohydrates consist solely of the condensation products of identical structural units while the fats have their component fatty acids attached to a common unit, namely, the trihydric alcohol-glycerol. In the case of fats, a further point of difference with the other two groups, is the peculiar complexity of the natural fats, based on their mechanical admixture or mutual solubility of their components.

How the fats are elaborated or what are their precise functions in the living plant is not known with certainty. However, the vital importance of the fats is evident from their presence in every cell of the reproductive organs such as seeds and pollen grains and their intimate association with substances like vitamins, sterols etc., which are fat soluble and are known to influence the life processes in nature.

During the last thirtyfive years attention has increasingly been given to the study of fats. The initial difficulties based on non-availability of the methods and techniques for handling fats and later the complexities involved in their structure have gradually been got over, still quite a few points remain obscure.

Our present knowledge of the molecular structure of fats is extremely fragmentary. Nothing definite, as yet, is known about the various phases of their molecular structure. It is also not known with certainty that what are the chemical steps involved in the synthesis, breakdown and reconstruction of fats either in the plants or in the animals.

Therefore a study of these points is of some importance. But before these studies can properly be taken up a clear understanding of the nature and composition of the glycerides which make up a fat and of the fatty acids which make up any particular glyceride and their structural complexities is necessary.

The work in this thesis describes for the first time the composition of Anethum trifoliatum, a member of the Umbelliferae family. A systematic study of hypohalogenation of the acid Petroselinic and its isomer, a major component acid of the family, with hypohalous acids has been made. The results throw some light on the stereo-chemistry involved in the transformation of petroselinic and petroselaidic acids (cis- and trans-6:7-octadecenoic acids respectively) to 6:7-Dihydroxystearic acids by way of the intermediate epoxy and halorohydroxy compounds.

THEORETICAL

THE FATS

Ordinarily the term 'fat' is understood to represent the material insoluble in water having a characteristic oily or greasy feel and consistency and isolable from plant and animal tissues. In common usage the word 'fats' and 'oils' have been applied to the same kind of material, though the word 'oil' is ambiguous in chemical nomenclature. The only distinction that an oil is a liquid fat, is a physical one. This physical state may change spontaneously as a result of chemical treatment or alteration in the environments. The term 'oil' as used here differs fundamentally from the word 'oil' when used for other liquids and therefore to make a distinction between the two terms, fatty oil, or fixed oil, has come into use. The other liquids are called the mineral or essential oils. The word 'fat' in the language of the chemist means a substance mainly made up of the esters of higher fatty acids with glycerol. Occasionally these fatty acids may also be found in combination with other types of naturally occurring compounds. There seems an unanimity of

opinion about the terminology to be adopted in the classification of these natural products, though the names given to these products differ from country to country. At the present time the broader term 'lipid' is in more common use. This term includes fats and other ether-soluble substances extractable from the plant and animal sources. The latest classification of lipids generally adopted after Hilditch[1] is as under:

I. Compounds containing only carbon, hydrogen, and oxygen.

(i) Esters of higher fatty acids with glycerol-triglycerides.

(ii) Esters of higher fatty acids with higher aliphatic alcohols, sterols-ester-waxes etc.

II. Compounds containing other elements i.e. phosphorous and nitrogen besides carbon, hydrogen, and oxygen.

(i) Glycerophosphoric acid coupled with a nitrogen base and/or a carbohydrate-phospholipids.

(ii) The long-chain hydroxy-amino alcohol, sphingosine-sphingolipids

(a) Phosphoric acid derivatives-sphingomyelin

(b) Not containing phosphorous-cerebrosides.

Paul sabatier's[2] (1897) discovery of catalytic hydrogenation followed by Norman's[3] (1903) important observation that the liquid fats could be hydrogenated to solid fats, opened a new chapter of study and led to a rapid progress in oil technology. The attention given to this work was so great that fundamental chemistry of the fats was practically forgotten. This indifference to the fundamental work on fats may be traced to a general lack of interest in substances of complex and non-crystallisable nature. The neglect was so great that in 1924 Armstrong[4] was led to entitle the work in this field as a "Neglected chapter in chemistry" and advocate its study.

This advocacy of Armstrong marks the begining of an active period of work in fat chemistry. New techniques for the study of natural fats were soon developed and improved. During the recent years the realisation that the fatty acids undergo all the classical reactions of organic chemistry has found them extended industrial use and consequently gave a tremendous impetus to their more systematic study.

The complexity of fats is not only due to the wide variety of the materials present in them but also arises from the nature of the triglycerides themselves, which are the major components of the natural fats. It has been rightly pointed[5] out that the variety of lipids (fats) and the specificity of their chemical constitution is second only to those of proteins.

THE CHEMICAL CONSTITUTION OF NATURAL FATS

Fats are made up of a number of glycerides. Each individual glyceride is made of a number of acids. The determination of the nature and quantity of the component glycerides is the first problem. After this comes the determination of the nature, configuration and disposition of these acids in the glycerol molecule. This in turn needs the separation of the various individual glycerides of a fat, a task at once be set with difficulties on account of close similarities in the physical properties of the glycerides. The polymorphic forms and the mutual solubility of the glycerides are other properties which did not permit the isolation of the individual glycerides in any purity. Even where individual glycerides are known to have been obtained in some purity, the exhibition of the phenomenon of isomerism by the glycerides complicated the problem. Further, there are more than one fatty acids usually present in a glyceride. The nature of these acids varies in the chain length of their carbon atoms, degree of unsaturation and the configuration. These

problems made the separation and the quantitative estimation of the glycerides a difficult one. However, with the availability of the facilities of crystallisation at low temperatures, the development of the molecular stills and solvent partition technique, the isolation of an individual glyceride in a fairly pure form has been made possible. The first question which now arose was that of the configuration of the glycerides, a question evaded till recently as the compositions of the component glycerides of the natural fats were expressed for the most part in general terms. But now when the way has been opened for the unravelling of the structural pecularities of the natural fats, what is needed is the checking up of the postulated structures of nearly all the isolated products, by a comparision with the synthetic ones to be prepared by recent unambiguous methods. Considerable work is also needed to give a completely satisfactory picture of either the original structure present in natural fats or those which arise from such treatments as hydrogenation, selective absorption etc.

The constitution of natural fats (triglycerides) is usually studied either (a) by determining the structure of the component glycerides, or (b) by estimating the fatty acid composition of the fat as a whole.

The component glycerides.

The studies of the component glycerides so far made give only certain broad generalisations about their constitution. These generalisations have mostly been arrived at by Hilditch and his collaborators who have successfully developed a few methods of investigation also in this field. Their a work on plant and animal fats has revealed that only the mixed triglycerides are elaborated in nature. Consequently fats have been defined as a mixture of mixed triglycerides. The di-acid glycerides predominate in the natural fats and the glyceride structure is dependent only on the proportions of its various component acids. It is independent of the particular kinds of the fatty acids present.

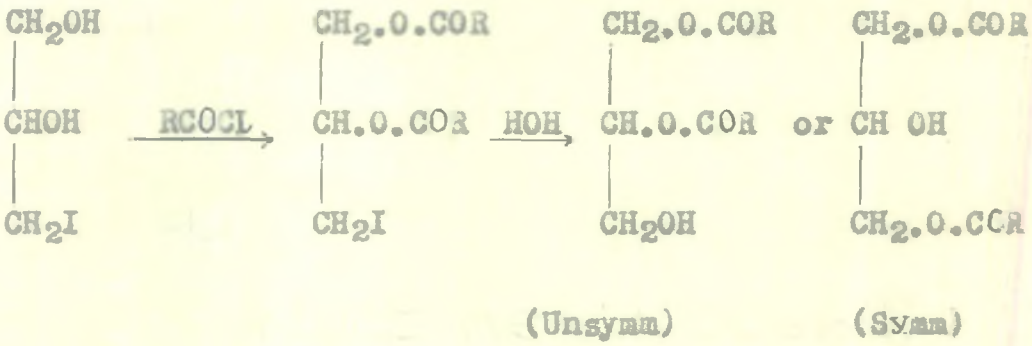
The specific configuration of glycerides in natural fats, despite considerable work, is but little known with certainty. The determination of the mode of distribution of various acids in the glycerides is still to be solved. The mechanism operating in nature which determines the composition of a fat is unknown.

A number of theories have been advanced from time to time to explain the pattern of glyceride distribution in the natural fats. The theory of "Even distribution" which originated from the researches of Hilditch and his school says that the fatty acids are distributed evenly and widely in as many glyceride molecules as possible. The theory holds good for the vegetable seed fats only. The animal depot fats rich in oleic acid and milk fats of the ruminants do not conform to the "Even distribution pattern". This limitation of the rule led to the postulation of other theories which are mostly modifications of the above theory. Longenecker[6] and Norris[7] put forward the "Random distribution" hypothesis which accounted for the mode of glyceride distribution in animal fats.

According to this hypothesis the difference in the mode of distribution in the plant and the animal fats may be ascribed to a basic difference in the synthetic action of the plant and the animal enzymes. This suggestion has support from the observation of Hilditch and Bhattacharya[8] "that mixed glycerides synthesised in vitro follow closely the random pattern of distribution". Two more theories, one proposed by Doerschuk and Daubert[9] called the "Partial random distribution" theory and the other by Kartha[10] known as "Restricted random distribution" theory, have also been suggested. All the above theories have been developed mostly from the analytical results obtained by hydrogenation, crystallisation and oxidation of fats. This state of things requires more work before a fully correct appreciation of the position can be made.

A review of the literature clearly shows that the present knowledge of the specific configuration of natural fats and their mode of distribution is uncertain. This uncertainty arises mainly on account of (a) the difficulties inherent in the isolation of an individual

glyceride in a pure form, (b) the existence of all glycerides in polymorphic forms (Malkin and Clarkson[11] have shown that the saturated as well as unsaturated glycerides, whether simple or mixed, exist in four solid forms) and (c) the unreliability of the earlier methods of synthesis, as it has been found now that the migration of an acyl group gives an unsymmetrical glyceride when a symmetrical one is expected.



(Unsymm) (Symm)

The methods recently developed for an unambiguous synthesis of glycerides of known configuration have opened a way for the correct identification of the natural glycerides. A comparision of the physical and chemical properties of the two sets of products, now promises to give definite results.

The component fatty acids.

The chemistry of fats is the chemistry of their fatty acids and therefore the estimation of the nature of these acids is the main point in the study of natural fats. The properties of the acids basically depend on the chain-length of their molecule, the degree of unsaturation, geometrical isomerism and upon the position of the double bonds with respect to carboxyl group and with respect to each other. These were the main points in their study and the difficulty in their isolation was the drawback in the analysis of the natural fatty acids. The isolation of an acid in a sufficiently pure state for a qualitative investigation has long been realised as a major problem in the work on fatty acid composition. The solution of all these problems was till recently attempted through the application of the method of crystallisation, a method, in itself, of limited analytical value on account of the phenomenon of molecular association and the formation of mixed crystals. Two other factors, the non-availability of facilities of working at low temperatures and

the misconception that unsaturated fatty acids are oily liquids were also responsible for a slow progress in the characterisation of the unsaturated fatty acids.

With the availability of improved and additional techniques for the separation of acids on the one hand and the development of new routes of synthesis on the other, it is possible to take up the work of characterisation of unknown acids with some confidence. The fixation of the configuration of familiar acids through ultra-violet and infra-red spectra and the realisation of the stereo-specificity of the reaction of isomeric acids opens the way for rapid progress in the field of familiar acids. The less familiar acids still pose a problem and unambiguous structures are not easy to arrive at.

Nevertheless progress has been made and certain generalisations have been drawn which hold good for a group of natural plant fats. One of these generalisations is that the naturally occurring saturated acids belong to the group of normal aliphatic acids. They always contain even number of carbon atoms ranging from

10 to 24 atoms in the molecule. Amongst these acids, palmitic (hexadecanoic, $C_{16}H_{32}O_2$) acid is the characteristic member and has been found to be the invariable component of all fats so far analysed. Myristic (Tetradecanoic, $C_{14}H_{28}O_2$) and stearic (Octadecanoic, $C_{18}H_{36}O_2$) acids are next to palmitic acid in their abundance of distribution in fats.

The natural unsaturated fatty acids in most cases belong to C_{18} series. The monoethenoid, oleic acid, is abundantly distributed in natural fats. The common polyethenoid C_{18} acids are linoleic (cis-cis-octadec-9, 12-dienoic) and linolenic (cis-cis-cis-octadec-9,12,15-trienoic) acids. The polyethenoid acids most frequently contain methylene interrupted unsaturation (i.e. pentadiene group - $-CH = CH - CH_2 - CH = CH -$) in their moleculeswhich is responsible for their characteristic reactions such as autoxidation and polymerisation. This reactivity of the pentadiene system has given importance to linolenic glycerides (drying oils) in the paint and allied industries. The polyethenoid acids having conjugated system are always triethenoid, the

only exception being linolenic acid. Further it has been observed that conjugated triene acids and their unconjugated counter-parts do not occur simultaneously in natural fats. A very interesting feature of the unsaturated acids is that either of the two molecular groups, $-CH_3(CH_2)_7.CH =$ or $= CH.(CH_2)_7.COOH$. (first and second half of the oleic acid molecule) is common to all C_{18} acids. This structural resemblance to the most common oleic acid itself suggests that they must surely have some relation to the chemical process by which these acids are synthesised from their carbohydrate precursor in the living plant. The highly selective process of the synthesis of unsaturated acids is also indicated by the exclusive preference for 9th. position for a double bond and for 12th. and 15th. positions for the subsequent double bonds.

Besides the common C_{18} unsaturated acids (oleic, linoleic and linolenic acids) other acids of unusual structure have been obtained from plant sources. The structure of these acids is unique in as

much as they posses either a triple bond or a hydroxyl group or an epoxide group or a cyclic ring in their molecules occurring singly or in combination. Another remarkable fact is the occurrence of all acids in cis form, which means that nature has a preference ~~s~~ for the elaboration of this form. Unsaturated acids with less than 10 carbon atoms have not so far been found in natural fats.

There is another fundamental difference in the mode of occurrence of saturated and unsaturated fatty acids. The unsaturated acids usually belong to the group of C_{18} acids, while any one saturated acid present as a major component is invariably accompanied by subsdiary proportions of saturated acids next higher and next lower in the homologous series. The fatty acid composition of all the fats is more or less confined to the universal occurrence of at least one saturated (palmitic) and two unsaturated (oleic and linoleic) acids. These three acids by virtue of their predominant occurrence have been designated as the "most characteristic acids" of seed fats.

led Hilditch[12] to suggest that the classification if made according to their fatty acid composition would almost be identical with that of their systematic botanical classification.

The structural diagnosis of the natural unsaturated fatty acids has always been a difficult problem in fat chemistry. The analytical methods are based mainly on reactions involving the oxidation and halogenation of fatty acids. The interpretation of the results of oxidation and halogenation experiments have been uncertain ones on account of the possibility of geometrical isomerism and isomerisation. It is now known that some of the reactions of isomeric fatty acids are stereospecific in nature so far as the configurational relation of the reactants and the products are concerned. Until this fact was fully appreciated the results of oxidation and halogenation studies were interpreted differently by different authors, and gave rise to a number of hypotheses and reaction mechanisms which were contradictory. Despite all the confusions, oxidation and halogenation methods continue to be the most important ones for the structural studies of unknown fatty acids.

The component acids of fruit coat-fats have also been studied mostly by ester-fractionation method of analysis. It has been observed that the general characteristics of all the fruit-coat fats are the same, the main components being palmitic and oleic acids. Further with the exception of linoleic acid, other component acids rarely form more than 2-5% of the total mixed fatty acids. The only exceptions to the statement are the fruit-coat fats of Myria species and some Lauracae fruits. There is no apparent connection between the general nature of the component acids of fruit-coat and seed fats.

It has been observed that the seed fats of a particular family are characterised by the presence of a group of acids which resemble both in qualitative and quantitative composition. It is interesting to note here that in the case of fruit-coat fats, the relation between the nature of acids and plant family does not exist. The most interesting observation that species with common morphological relationship produce qualitatively the same mixtures of fatty acids in their seeds,

OXIDATION OF UNSATURATED FATTY ACIDS

The studies in the oxidation of unsaturated fatty acids were primarily initiated for the purpose of elucidating the structure of these acids. The realisation that these studies are of fundamental importance in such processess as the utilisation of fats in the animal body, the drying of oil films, and in the spoilage of fats, came later.

The oxidising agents which have been used in fat chemistry are generally the same as used in the study of any other series of organic compounds. The oxidised products are numerous and diverse in nature. The remarkable property of the oxygenated products of being low-melting and of easy crystallisability, has been very helpful in the detailed study of oxidation reactions. The fact that the oxygenated acids are usually found to be the essential intermediates in autoxidation, chemical oxidation and studies of reaction mechanisms, aroused considerable interest in their studies. The importance of oxygenated fatty acids in the drying oil industry realised during the last 25 years gave added interest to the study of the oxidation processes.

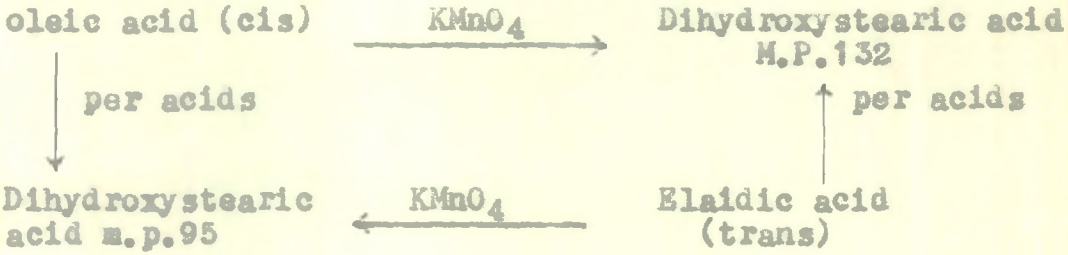
The nature of oxygenated fatty acids produced depends primarily on the class (mild or drastic) of the oxidising agent used and the conditions under which the oxidation is carried out. The numerous and diverse products obtained from the oxidation of an acid have always been a drawback in arriving at a definite conclusion and therefore despite the vast amount of data available in literature on oxidation products no single generalisation about the mechanism of oxidation had found general acceptance.

On the basis of the oxidation products the oxidation reactions may be classified into 3 types, (a) hydroxylation, (b) epoxidation, and (c) degradation.

(a) Hydroxylation:

The hydroxylation of unsaturated acids to the corresponding polyhydroxy acids (glycols) has long been used for the identification of the unknown fatty acids. The early and most widely used reagents were alkaline potassium permanganate and performic acid. The hydroxylation of isomeric unsaturated acids by these reagents

resulted in the formation of an isomeric pair of glycols. The potassium permanganate hydroxylation of the cis-acid yielded the high-melting hydroxy acid while that of the trans-acid gave the low-melting derivative. The products were reversed when performic acid was used for hydroxylation as under:

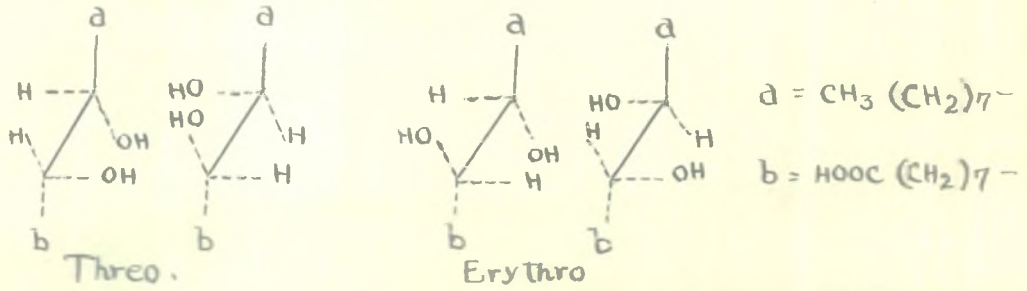


The formation of these isomeric pairs of glycols from a given pair of isomeric unsaturated acids, at one time, gave rise to a great controversy about the configuration of the hydroxylated products. The actual mechanism involved in the formation of isomeric dihydroxy acids from mono-ethenoid acids is still not known though considerable experimental work has been done. It is now known that hydroxy acids found are not geometrical isomers but are the racemic forms. Swern[13] in 1948

proposed a reaction scheme which correlated the configurational relationship in the conversion of oleic and elaidic acids to 9:10-dihydroxystearic acids. He suggested that the isomeric dihydroxy stearic acids are not geometrical isomers but are diastereo-isomers. According to his scheme alkaline permanganate hydroxylation proceeded by a cis-addition to double bonds. Further he assumed that the initial step of the peracid hydroxylation was the formation of an epoxide by cis-addition. The hydrolysis of the epoxides to the corresponding glycols was accompanied with the inversion in the configuration. This is the reason why opposite isomers are obtained in the case of peracid hydroxylation. In other words the hydroxylation with peracids is equivalent to the trans-addition of hydroxyl group to the double bonds.

Recently Gunstone and coworker [14] have suggested that the usual designation of cis- and trans-configurations to glycols is confusing and that the terms "threo" and "erythro" should be applied in such cases. This terminology will also give proper representation of the

absolute configuration of the glycols. The compounds obtained by the trans-addition to a cis- or cis-addition to a trans-ethylenic compound are designated as "threo" isomers, where as the products of cis-addition to a cis- or trans-addition to a trans-unsaturated compound are named as "erythro", isomers. The two structures of the dihydroxystearic acids may be represented as under[15];

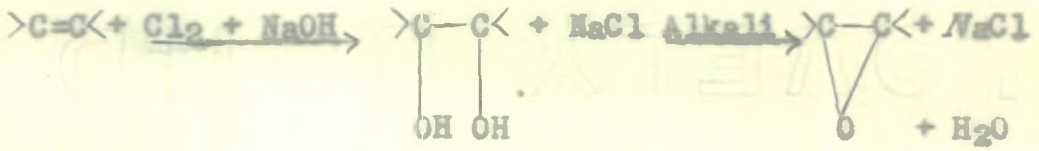


The other hydroxylation reagents not so frequently used are iodine and silver acetate, and potassium manganate. The former reagent was originally used by Woodward[16] in the case of alicyclic compounds. Recently Gunstone et al[17] and Farooq and coworker[18] have also successfully applied the reagent for the hydroxylation of long-chain fatty acids.

When, however, the permanganate oxidation is carried out in almost neutral medium the principal products are the hydroxy keto-acids. A systematic study of the simple ∝-ketols of stearic acid derived from oleic and elaidic acids was first carried out by King[19]. Later Farooq and coworker[18] studied the isomeric pair of the acids petroselinic and petroselaidic.

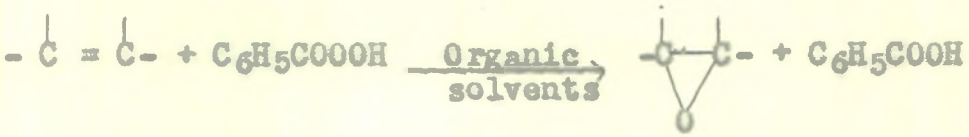
(b) Epoxidation.

The term epoxidation usually refers to the process of oxidation which exclusively results in the formation of epoxides (Oxiranes). The classical method of preparing an oxirane is the hypochlorination of an unsaturated compound and its subsequent dehydrohalogenation.



The method of the chlorohydrin synthesis[20,21] of epoxides is comparatively a tedious one and the yield of the epoxides are generally poor.

Another successful method was evolved by Prileschajew[22] who showed that the olefinic compounds containing isolated double bonds could be subjected to epoxidation with perbenzoic acid according to the following course of reaction:



This discovery opened a way for a search for other organic peracids suitable for the preparation of oxiranes. Considerable work was subsequently done on the reaction of unsaturated acids with organic peracids by Boeseken[23], Smit[24], Bauer and Bahr[25] and Arbusow and coworker[26]. The oxidation in acetic acid medium with peracetic acid results in the formation of glycols or of the monoacetates whereas epoxides are only formed when the reaction is carried out in the presence of inert solvents. Swern and collaborators[27] have reported that the oxirane ring opens easily to form the glycols when the epoxidation is conducted either at a short reaction time at high temperatures or a longer reaction time at

low temperatures. A more suitable condition for the formation of epoxides is that the reaction should be carried out only over 2 to 4 hours at room temperature using from 1.1 to 1.2 moles of peracetic acid per mol. of the double bond. In addition to the peracids described above, monoperphthalic acid has been successfully used in the preparation of oxiranes. Chakravorty and Levin[28] were the first to achieve a successful epoxidation by this reagent. Later it has been extensively used in the field of sterols and polyenes. Recently Farooq and collaborator[29] have used monoperphthalic acid and peracetic acid for the epoxidation of isomeric 6:7-octadecenoic acids.

The epoxidation reaction is stereospecific in nature i.e. the geometric configuration of the epoxide is similar to that of the parent acid. Swern and Witnauer[30] have reported on the basis of infra-red spectra and X-ray diffraction studies that cis-olefinic compounds on epoxidation with peracetic and perbenzoic acids yield cis-epoxy derivatives whereas trans-epoxy compounds are obtained from trans olefins. The obser-

vation that the configuration of the acids remain intact during epoxidation has been further confirmed by Farooq and coworker[29]. The authors have shown from the infra-red spectra that the epoxides of petroselinic and petroselaidic acids posses the cis- and trans-configurations respectively.

(c) Degradation.

The oxidative cleavage of the molecules of fatty acids by the application of drastic oxidising agents have long been used for their structural diagnosis. Solid potassium permanganate and ozone are the two oldest reagents used. The oxidative studies with periodic acid and lead tetra-acetate for the solution of structural problems and of reaction mechanisms have been developed only in recent years and are still under close examination. The Criegee's[31] lead tetra-acetate oxidation reaction is highly specific and cleaves the molecule between the two adjacent carbon atoms carrying the hydroxyl groups. It can be successfully used in the location of the position of the double bond in unsaturated fatty acids by previous hydroxylation of such bonds

as illustrated below:

$$CH_3.(CH_2)_7CH{=}CH\ (CH_2)_7COOH \xrightarrow{KMnO_4} CH_3(CH_2)_7\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_7COOH$$

Oleic acid — Dihydroxystearic acid m.p. 132°

$$Pb(OAc)_4 \longrightarrow CH_3(CH_2)_7CHO + OHC(CH_2)_7.COOH$$

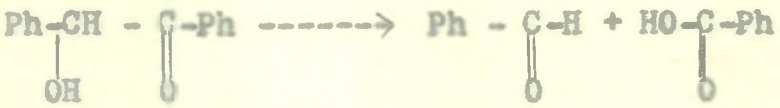
n-Nonanal — Azelaic semialdehyde

Criegee and coworkers have further shown that lead tetra-acetate could also be applied in strictly anhydrous condition to the cleavage of ∝-hydroxy acids[32] as under:

$$R\text{-}CHOH\text{-}COOH \xrightarrow{Pb(OAc)} R\text{-}CHO + CO_2$$

It was in 1939, for the first time, that Baer and collaborators observed that this reaction in moist organic solvents can be used for the cleavage of ∝-ketonic acids and ∝-hydroxy ketones as described below:

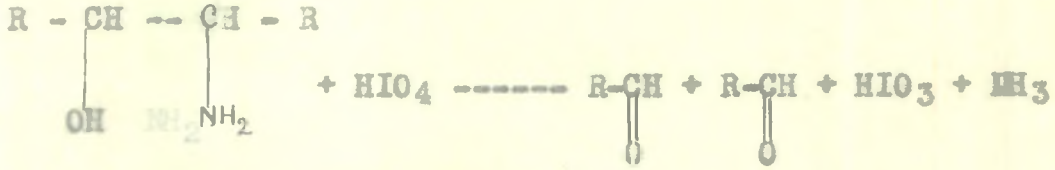
$$Ph\text{-}CO\text{-}COOH + Pb(OAc)_4 + H_2O \longrightarrow Ph\text{-}CO.OOH + Pb(OAc)_2 + 2CH_3COOH.$$



They have suggested that the use of lead tetraacetate to split ∝-keto acids and ∝-keto alcohols may solve some of the problems concerning chemical constitution or tautomerism. Recently it has been shown by Farooq and coworker[18] that lead tetra-acetate in 70% acetic acid is an effective cleavage reagent for 1,2-ketols and 1,2-diketones. The isomeric pair of 6(7)-hydroxy-7(6)-ketostearic acids obtained by the neutral permanganate oxidation of petroselinic acid (cis-6:7-octadecenoic acid) have been characterised by the identification of the fission products of lead tetra-acetate oxidation.

Another cleavage reagent is periodic acid ($HIO_4.2H_2O$) which has been widely used in the disruptive oxidation of 1,2-glycols[34] ∝-ketols, ∝-diketones and ∝-ketonic aldehydes. Besides these compounds, others with a hydroxyl group and an amino group attached to

vicinal carbon atoms, also react with periodic acid as under[35]:



The cleavage does not take place when the hydroxyl groups or a hydroxyl and an amino groups are not vicinal. This selectivity is the unique characteristic of periodic acid oxidation. This procedure has been succesfully applied by King[19] to determine the constitution of isomeric 9(10)-hydroxy, 10(9)-keto-acids. More recently Gunstone[36] applied this method to locate the position of the epoxy group in the naturally occurring 12:13-epoxyoleic acid.

H A L O G E N A T I O N

Halogen addition reactions are an important class of reactions in the diagnosis of unsaturation and its estimation. The halogen addition products have been of immense help in the characterisation of unsaturated compounds. They have also been of help in the isolation of unsaturated compounds in the pure form. Halogen addition reactions as such have also been used in fat chemistry specially for the identification of unsaturated fatty acids and their isolation in a pure form. These addition compounds also serve as intermediates in the preparation of more desirable derivatives of the fatty acids. A review of the literature shows that only a few systematic investigations of the halogenation products of fatty acids have been made and amongst them some of the halogenated products are of doubtful purity and therefore of doubtful value. The cause for this impurity arises out either from the non-homogenity of the parent acids or on account of the contamination of the main products with subsidiary reaction products.

Not only halogens but hypohalous acids also add on to the unsaturated acids and therefore they have also been used particularly in the mono-ethenoid series of fatty acids. The importance of hypohalogenation in the configurational studies of the unsaturated fatty acids has now been realised for sometime. The halohydrins give easily the epoxides which on treatment with alkali yield the corresponding isomeric hydroxy acids.

Hypohalogenation.

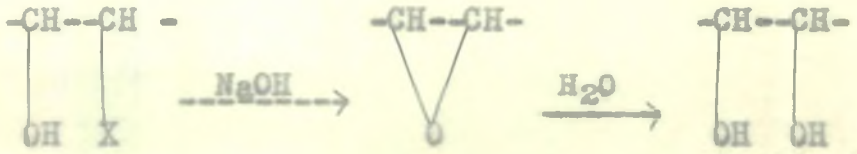
Hypochlorous, hypobromous and hypoiodous acids add directly to the ethylenic double bonds of the unsaturated acids to form the corresponding halohydrins, thus:

$$\text{--CH = CH--} + \text{HOX} \longrightarrow \text{--CH(OH)--CH(X)--}$$

The halohydrins except as intermediates in the preparation of the epoxy- and poly-hydroxy acids have no practical value and therefore attracted less attention earlier. Most of the investigators who have

studied the addition products of the higher unsaturated acids with hypohalous acids were concerned with the problems of isomerism.

The hypohalogenation reactions resemble hydrohalogenation reactions. The hypohalous acid functions as $HO^{+}X^{-}$, and the direction of addition to an ethylenic bond is subject to the same considerations as in additions involving halogen halides. When treated with aqueous or alcoholic alkalis the halohydrins are converted to epoxides, which on hydrolysis yield the dihydroxy acids.

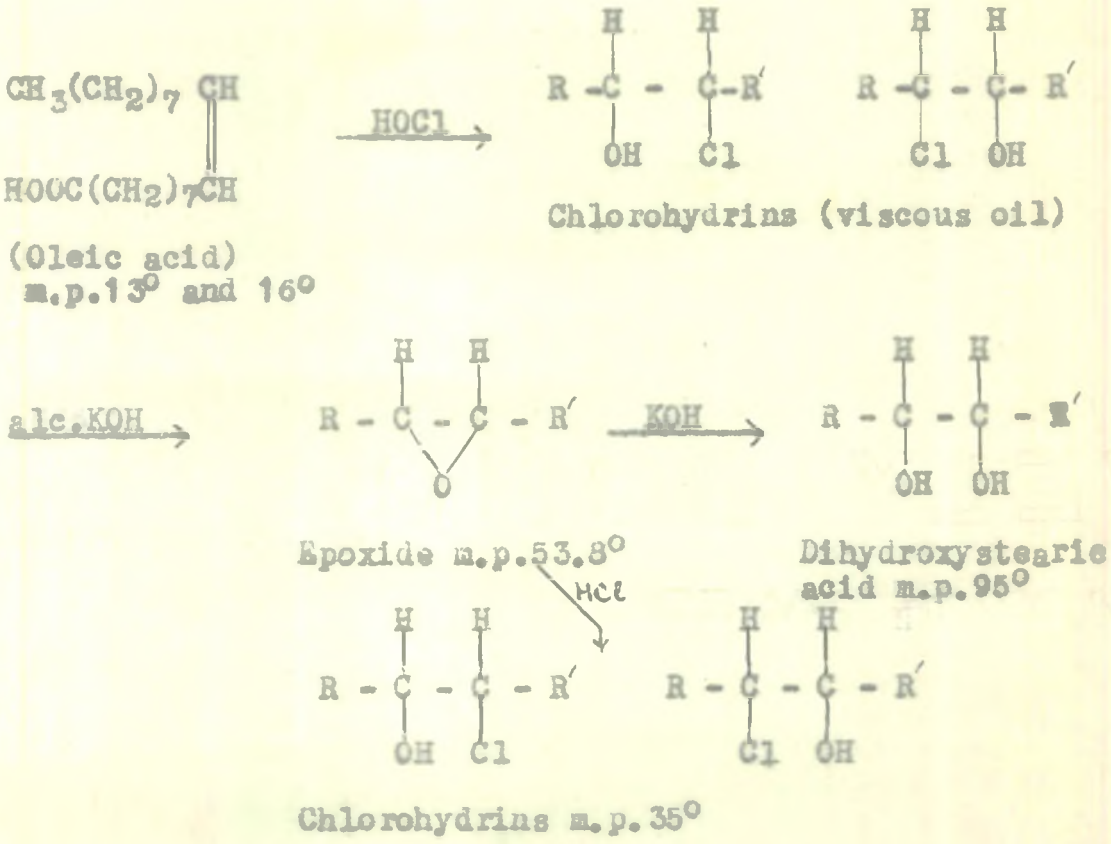


The mechanism of the addition of hypohalous acids to, and their removal from, double bonds, was for a long time not clearly understood. The configurational changes involved in the preparation of oleic and elaidic acids via the intermediate epoxy and chlorohydroxy acids had been a subject of considerable discussion over a number of years.

Extensive investigations of the hypohalogenation reaction were reported by Albitzky[37] more than fifty years ago. He prepared a series of addition products of oleic, elaidic and erucic and brassidic acids. But his work, though comprehensive, suffered from the fact that the unsaturated acids which he used were not of desired purity. The correct configurations of these acids were unknown at that time. The significance of some of the reaction products was not recognised. Albitzky prepared the halohydrins by the addition of hypochlorous or hypobromous acids to the alkali salts of the unsaturated acids obtaining halohydrins as viscous oily liquids.

Nicolet and Poulter[21] in 1930 showed that the chlorohydrins of oleic and elaidic acids can be prepared by carefully controlled action of chlorine on solutions of their potassium salts containing potassium carbonate. The chlorohydrins obtained in this manner were uncrystallisable viscous oils and considered by Nicolet and Poulter to be similar to those obtained by Albitzky by the addition of hypochlorous acid.

In order to discuss the probable identity of chlorohydrins it is necessary to refer to their epoxy and dihydroxy conversion products. Nicolet and Poulter[21] refluxed the chlorohydrins of oleic and elaidic acids for two hours with an excess of sodium ethylate in 95% alcohol, whereby the acids were converted into the corresponding epoxides. Treatment of the epoxides with aqueous alkali or acid resulted in slow hydrolysis and the production of the corresponding dihydroxy acids. Only the low melting dihydroxystearic acid was obtained from oleic acid epoxide and only the high melting dihydroxystearic acid was obtained from the elaidic acid epoxide. The treatment of the epoxides of oleic acid and of elaidic acid with dry hydrogen chloride in dry ether resulted in the regeneration of chlorohydrins, but unlike the original chlorohydrins from which the epoxides were formed, they were obtained as solids melting at 35° and 50° respectively. Nicolet and Poulter[21], therefore, concluded that the original chlorohydrins were 9-chloro-10-hydroxystearic acids, while those regenerated through the epoxides were 9-hydroxy-10-chlorostearic acids.



In studies of the products of hypohalogenation and their conversion first to the epoxides and then to the dihydroxy acids, the possibilities of configurational changes (inversions) must be taken into consideration. Further, it appears that hypochlorous acid or hypobromous acid should add to the double bond of oleic or elaidic acids, preferentially to produce specifically either the 9-halo-10-hydroxy (I) or the 10-halo-

9-hydroxy (II) stearic acids or an equilibrium mixture of the two isomers as under:

$CH_3.(CH_2)_7-CH=CH-(CH_2)_7-COOH$

Oleic acid

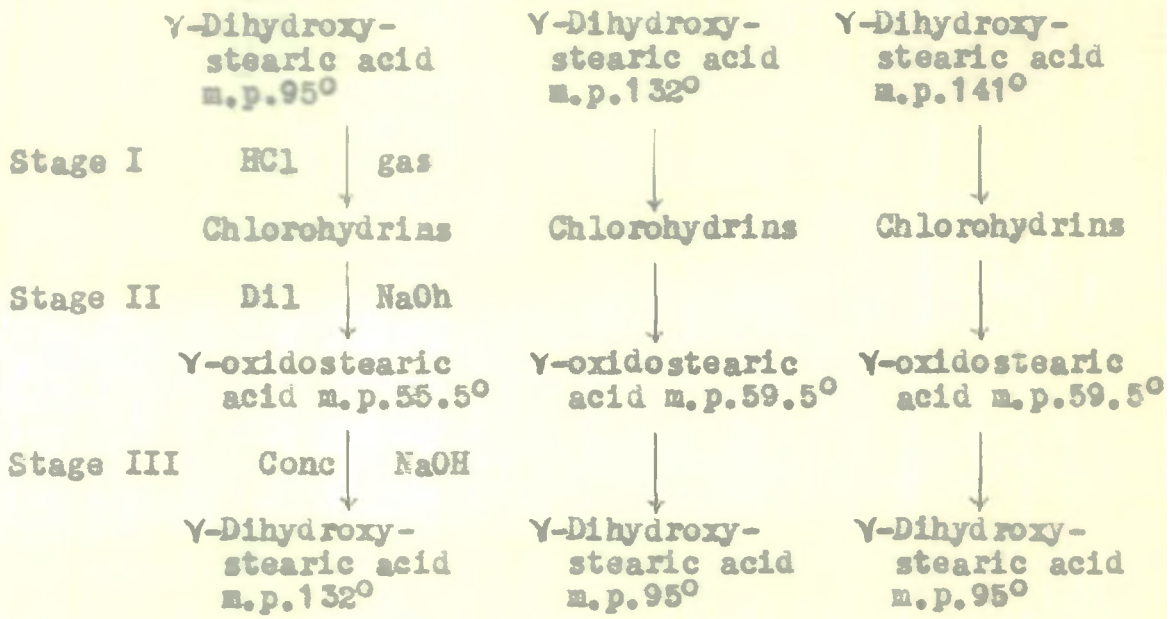
$\xrightarrow{HOCl}$

$CH_3(CH_2)_7-\underset{OH}{CH}-\underset{Cl}{CH}-CH_2)_7.COOH$ (I)

+ $CH_3(CH_2)_7-\underset{Cl}{CH}-\underset{OH}{CH}-(CH_2)7.COOH$ (II)

Untill these facts were appreciated hypohalogenation studies frequently resulted in erroneous conclusions regarding the identity of the reaction products.

King[38] (1942) made a detailed study of the stereochemical relationships of the dihydroxy acids which were obtained by their interconversions through the corresponding chlorohydrins and oxidostearic acids as given below:



King[38] showed that either of the 9;10-dihydroxystearic acids m.p.132° or 95° furnish the opposite isomeride (95° or 132° respectively) after conversion by hydrogen chloride into chlorohydrins, formation of epoxides from latter, and subsequent opening of the epoxide ring. He concluded that a Walden inversion takes place during the course of the hydrolysis of the epoxy compound to the dihydroxystearic acid.

Just a year after King's work Hilditch and Atherton[39] investigated this question of inversions in the above transformations. They found that when either of the two forms was treated with an ethereal solution of hydrochloric acid the oxido ring is opened and chlorohydroxystearic acids are produced. Further these

chlorohydroxy acids in presence of alkali undergo ring closure with the formation of the same epoxy acids. They suggested that there is no inversion either during the opening or of the closing of the epoxy ring, or that the inversion takes place during both of these processes.

They have also observed that the inversion which occurs when either of the dihydroxy acids is converted into chlorohydroxy acids, must take place during replacement of a hydroxyl group by chlorine. It is interesting to note here that the configurational schemes, provisionally assigned to explain the course of transformation, by Hilditch[39] and by King[38] are different.

The above problem received no attention till the year 1948 when Swern[13] from purely general considerations and from the facts of the earlier observations, proposed a reaction scheme. This scheme correlated the configurational relationships in the conversions of oleic and elaidic acids to their corresponding glycols through alternative routes. He

claimed that the scheme was self consistent and was in harmony with the accepted theories of Walden inversions and addition to double bonds. According to his hypothesis the reaction of ethylenic acids with hypohalous acids proceeded by a trans-addition to the double bonds. It has been postulated that inversion in the configuration takes place during the hydrolysis of the epoxide ring. Further, the inversion also takes place during the course of dehydrohalogenation (closing of the epoxide ring). This scheme satisfactorily explains the identity of the epoxides for either by organic peracids or by hypohalogenation followed by dehydrohalogenation (as described later in the reaction scheme).

An extensive and detailed study of the stereochemistry of halohydrins was made again in 1949 by King[40]. He investigated the addition of hypochlorous, hypobromous and hypoiodous acids to oleic and elaidic acids and studied the conversions of halohydroxystearic acids to epoxy acids and the hydrolysis of the epoxides. He concluded that an inversion accompanies each of the following three stages.

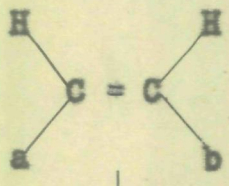
(a) the addition of hypohalogen acid to a double bond,

(b) dehydrohalogenation of the halohydroxy acids with the formation of the epoxide and,

(c) opening of the epoxide ring.

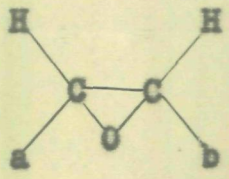
The reaction scheme suggested above is in conformity with the mechanism proposed by Swern. The accepted reaction scheme which correlates the configurational relationships in the conversion of oleic and elaidic acids to the isomeric 9:10-dihydroxystearic acids by way of the intermediate epoxy and chlorohydroxy compounds is described below:

1. Oleic acid



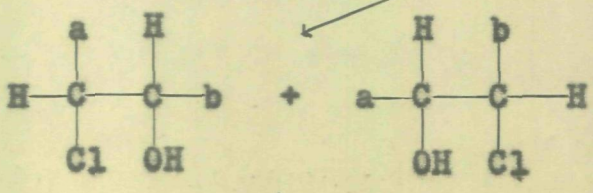
Org.peracids (cis-addition)

2. 9:10-Epoxy acid m.p.59.5°



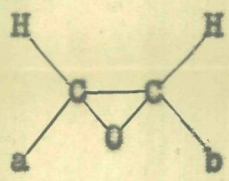
Reaction with HCl (inversion)

3. 9:10(10:9)-chlorohydroxy acids m.p.39°



Splitting out of HCl (inversion)

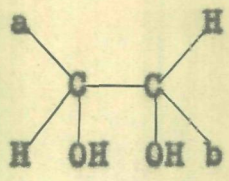
4. 9:10-Epoxy acid m.p.59.5°



Identical with 2.

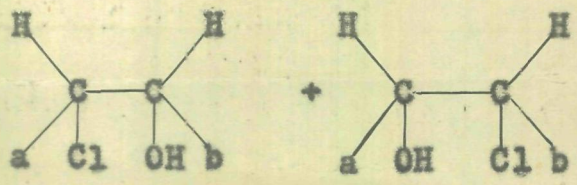
Alkaline aqueous hydrolysis (inversion)

5. 9:10-dihydroxy acid m.p.95°



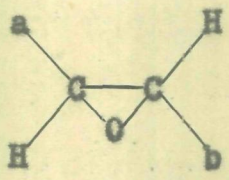
Reaction with HCl (inversion)

6. 9:10(10:9)-chlorohydroxy acids m.p.58°



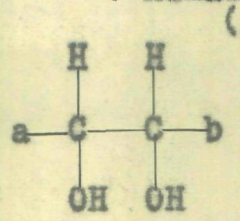
Splitting out of HCl (inversion)

7. 9:10-Epoxy acid m.p.55.5°



Alkaline hydrolysis (inversion)

8. 9:10-dihydroxy acid m.p.131°



Reaction with potassium permanganate (cis-addition)

A review of the work on hypohalogenation of unsaturated fatty acids clearly brings out the fact that more experimental data is necessary to ascertain the correctness of various mechanisms postulated to explain the configurational changes involved in the addition of hypohalous acids to, or their removal from, the double bonds of the organic compounds. The studies so far made on the hypohalogenation are confined only to one isomeric pair of C_{18} unsaturated acids, oleic and elaidic. With a better knowledge of stereospecificity of certain reactions, it is now possible to have a greater stereo-chemical control over configurations of the reaction products.

The thesis describes the work on the seed fat composition of two members of the family Umbelliferae and three members of the family Leguminosae. It also describes the work on seed fat of Haloptela integrifolia, a member of Urticacae family. Most of this work has been published and is given in the papers attached at the end of the thesis.

The thesis also describes the result of a systematic study of the hypohalogenation on the less familiar isomeric pair of C_{18} acids, petroselinic and petroselaidic. These acids were readily available in the laboratories, having accumulated in large quantities during the course of the work on the seeds of the members of the family Umbelliferae.

THE SEED FATS

OF

(i)	Seseli indicum	Family	Umbelliferae
(ii)	Anethum trifoliatum	"	"
(iii)	Albizzia odoratissima	"	Leguminosae
(iv)	Albizzia procera	"	"
(v)	Leucaena glauca	"	"
(vi)	Haloptela integrifolia	"	Urticacae

The seed fats of the members of the family Umbelliferae.

Vongerichten, and Kohler[41] reported the presence of petroselinic acid (6:7-octadecenoic acid, a positional isomer of oleic acid) in a high yield (70%) in the parsley seeds. It was the first report of the presence of this acid in a natural fat and drew attention to the fats of the members of the family. Since then considerable effort has been devoted to the seed fats of the members of this family. Hilditch et al[42,43,44], van Loon[45], Menon and Raman[46], Kurono et al[47] and Farooq and coworkers[48,49] have all shown that in most of the seed fats of this family, petroselinic acid occurs in abundance. The other unsaturated acids reported in these fats are the ordinary oleic and linoleic acids and were found to occur in varying proportions. The only saturated acid present in these fats is palmitic acid, which occurs as a minor component acid.

The comparative insolubility of lead-salt of petroselinic acid in alcohol compared to that of the lead-salt of oleic acid has been utilised in the separation and a quantitative estimation of this acid. According

to Hilditch[43] "the separation of petroselinic acid from other C_{18} unsaturated acids by the lead-salt alcohol method is sufficiently marked and a reasonably accurate estimation of the petroselinic content of a fat can be made". Meara[50] also remarks about the helpfullness of this method for the estimation of petroselinic acid in Umbelliferae seeds. The presence of petroselinic acid has also been reported in the seed fats of two other families namely Araliacae and Simarubacae.

The fatty acid composition of the seed fats of Seseli indicum and Anethum trifoliatum have been detsrmined in the present work by the usual ester-fractionation method using the two groups of fatty acids, "solid" and "liquid", separated by Hilditch's modification of the Twitchell's lead-salt alcohol method[51]. The temperature was carefully kept at 15° during the course of all lead-salt separations[52] of the mixed fatty acids. The seed fats were purified and freed from resinous matter prior to their analysis.

The identification of the individual acids present in a fat have been made by their melting points and also by the preparation of some of their derivatives. The percentage of individual acids in ester-fractions were

calculated by the Iodine value and saponification equivalent figures taken in conjunction with the qualitative data of the ester-fractions.

The Seed Fats of the Family Leguminosae.

The seed fats of the family Leguminosae are characteristic in having specific saturated acids (arachidic, behenic and lignoceric) as major components in addition to the common palmitic, oleic and linoleic acids. It has been suggested by Hilditch[53] that due to the presence of specific saturated fatty acids in these fats, the family Leguminosae, particularly its sub-family Mimosacae, may prove a very interesting field for further investigation of the component acids of the seed fats. In contrast to the seed-fat of Mimosacae sub-family, the fat of the other two sub-divisions of the Leguminosae (Caesalpinioidae and Papilionatae) do not have large proportions of C_{20} to C_{24} acids.

The seed fats of this family have been shown to possess two types of component acid mixtures. In one group the saturated C_{20}, C_{22} and/or C_{24} acids are present in amounts from 6 to 15% of the total acids, with 5-8%

of palmitic and a smaller amount of stearic acid. In other group the quantity of palmitic and stearic acids is higher (nearly 15%) and the amount of higher saturated acids is almost negligible in as much as that only one and in some cases two of the three C_{20}, C_{22} and C_{24} acids are present. However, there seems to be no sharply defined boundary between them. These variations may possibily be due to the biological variations as suggested by Hilditch[57].

A further point of interest in the work on the Leguminosae seed fats arose from the fact that their seeds were being investigated in these laboratories for their saponin[54] contents.

NEW WORK

Family Umbelliferae (Seseli indicum and Anethum Trifoliatum.)

The results of the fatty acid composition of these fats are given below:

TABLE I.

Acids.	Seseli indicum.	Anethum trifoliatum.
Palmitic	6.18	9.37
Petroselinic	46.06	48.85
Oleic	30.96	33.90
Linoleic	13.80	7.88

The conclusions based on these results are summarised below:

These results on Anethum trifoliatum and Seseli indicum are in line with the findings of all other investigators on the seed fats of the members of the family Umbelliferae i.e. the presence of petroselinic acid as a major component acid, appreciable amount of resinous matter, low saponification value, high contents of unsaponifiable matter and the presence of palmitic acid as the only saturated acid.

Family Leguminosae (Albizzia Odoratissima, Albizzia Procera and Leucaena glauca).

The fatty acid composition of these seed fats examined by the author are summarised in Table II.

T A B L E II.

Acids	Albizzia odoratissima.	Albizzia procera.	Leucaena glauca.
Saturated.			
Palmitic	14.33	7.23	12.74
Stearic	6.88	14.26	5.01
Arachidic	0.81	12.21	-
Behenic	-	-	3.64
Lignoceric	-	-	0.67
Unsaturated.			
Oleic	26.56	50.89	23.63
Linoleic	51.42	15.41	54.31

The result of the above work leads to the following points:

(i) The presence of specific saturated acids in these fats confirm the generalisations regarding the Leguminosae seed fats in which one or more of the higher fatty acids are usually present.

(ii) The main components of the total fatty acids are the C_{18} unsaturated acids, oleic and linoleic. The preponderant occurrence of these acids to the extent of 60-80% of the total fatty acids coroborates Hilditch's[55] generalisation that Leguminosae seed fats in this respect resemble the simple 'linoleic-oleic-palmitic' type of fats.

(iii) The absence of linolenic acid in these fats is in conformity with the earlier findings that this acid is not at all present in the Leguminosae seed fats so far examined.

Fatty acid composition of the seed fat of Haloptela integrifolia (N.O. Urticaceae).

During the course of the above work on indigenous seed fats the attention of the author was drawn to the

seed fat of Haloptela integrifolia. The seed fat of this plant is used for edible purposes. Even the seeds as such as cherished by children and cattle.

Well powdered, air-dried seeds, on petrol extraction gave 50% of fat. The fat very much resembles the cow milk fat in appearance. The fatty acid composition by the procedure earlier recorded was estimated as under:

Saturated acids.

Palmitic	37.64
Stearic	10.04
Arachidic	2.03

Unsaturated acids.

Oleic	46.66
Linoleic	3.63

It is of interest to note here that a few seed fats of the family Urticaceae earlier examined contain fatty acids where the ratio of saturated to unsaturated is 1:12 while in this seed fat the ratio is about $1:1^{56}$. Further the extraordinary high palmitic acid content (37.64%) of this seed fat is remarkable and accounts for its consistency in which it resembles the cow milk fat. However, the high fat content of the seeds and the consistency of this fat attracts attention for its utilisation as an edible fat.

Studies on the Hypohalogenation of the isomeric 6:7-Octadecenoic acids.

Hypochlorination:

The hypochlorination of petroselinic and petroselaidic acids was carried out,

(a) by sodium hypochlorite solution and,

(b) by chlorine water

6(7):7(6)-chlorohydroxystearic acids from petroselinic acid.

Petroselinic acid on hypochlorination with a solution of sodium hypochlorite in presence of potassium hydroxide yielded 50-55% of a mixture of the two isomeric (6(7):7(6)-chlorohydroxystearic acids m.p. 50-55°. This melting point on twice recrystallisation from methyl alcohol was raised to 59-60°.

When the hypochlorination was carried out with chlorine water, it was found that a small amount (15-20%) of 6(7):7(6)-chlorohydroxystearic acids was easily isolable which on further purification from aqueous methyl alcohol melted sharply at 59-60.

A determination of the mixed melting point of the 6(7):7(6)-chlorohydroxystearic acids obtained through the action of sodium hypochlorite with those prepared by using chlorine water, showed no depression thus confirming the identity of the two products.

The chlorohydroxy acids on dehydro-halogenation by treatment with alkali readily afforded a nearly theoretical yield of 6:7-epoxystearic acid m.p. and mixed melting point with a genuine sample 59-60°.

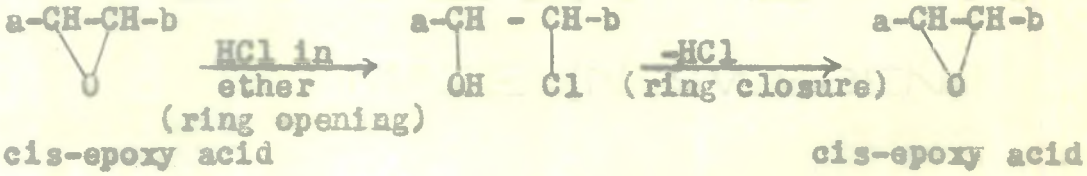
Petroselinic acid m.p. 30° —HOCl→ 6(7):7(6)-chlorohydroxystearic acid m.p. 59-60° —Alkali (HCl)→ 6:7-epoxystearic acid m.p. 59-60°.

6(7):7(6)-chlorohydroxystearic acids from 6:7-epoxystearic acid.

6:7-epoxystearic acid (petroselinic acid epoxide) in ether solution readily reacted with concentrated hydrochloric acid to give a mixture of 6(7):7(6)-chlorohydroxystearic acids m.p. 53-56°. On repeated crystallisations a fairly pure mixture of chlorohydroxy acids melting at 59-60° was obtained. It showed no depression

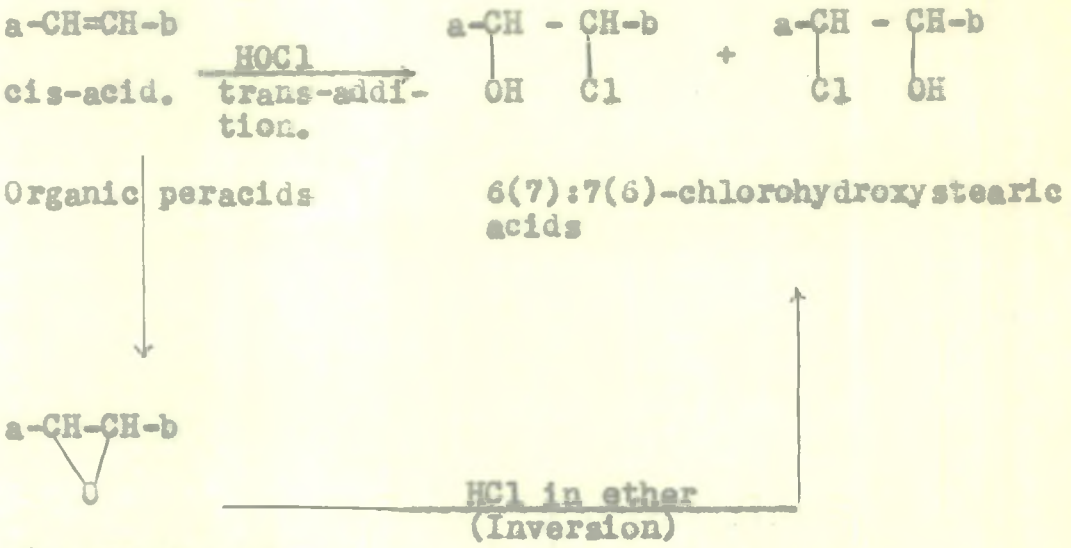
when mixed melt with samples of acids obtained by the use of either sodium hypochlorite solution or chlorine water.

The treatment of these chlorohydroxy acids with alkali yielded the original epoxide from which they were prepared as represented below:



cis-epoxy acid cis-epoxy acid

It has been earlier pointed out that the reactions of hypohalous acids proceed by a trans-addition to the double bonds of ethylenic acids and that the epoxidation reaction is stereospecific in nature. In the light of these reaction mechanisms the foregoing results may be systematically represented as below:



Thus, the chlorohydroxy acids, obtained from the cis-acid (petroselinic acid) with hypochlorous acid and those obtained by the epoxidation of the cis-acid and subsequent treatment of the epoxide with hydrochloric acid, are indentical. The identity of the chlorohydroxy acids is of considerable importance from the point of view of configurational relationships in the formation of halohydrins and their conversion to epoxides.

The fact leads at once to the conclusion that inversion in the configuration does occur during the reaction of the epoxide with hydrochloric acid (i.e. on the opening of the epoxide ring on hydrohalogenation)

and negatives the suggestion of Nicolet and Poulter*, and supports the findings of King**. Further, this also goes contrary to the conclusion of Hilditch and Atherton, who postulated no inversion during either the opening or the closure of the epoxy ring.

Finally, this fact provides additional experimental evidence in support of Swern's general reaction scheme described earlier (page 43)

The identity of the two epoxides could only be explained if the inversion during the closure of the ring is allowed for. This means that the inversion takes place both during the opening as well as of the closing of the epoxy ring.

6(7):7(6)-chlorohydroxystearic acids from petroselaidic acid.

It has been found that hypochlorous acid in aqueous solution adds on to petroselaidic acid and gives 55-60%

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* The authors having earlier suggested that these chlorohydroxyacids differ, one of them possibly being the 9-hydroxy-10-chloro and the other 9-chloro-10-hydroxy-stearic acid.

** King suggested the possibility of inversion both in the opening and the closing of the epoxy ring.

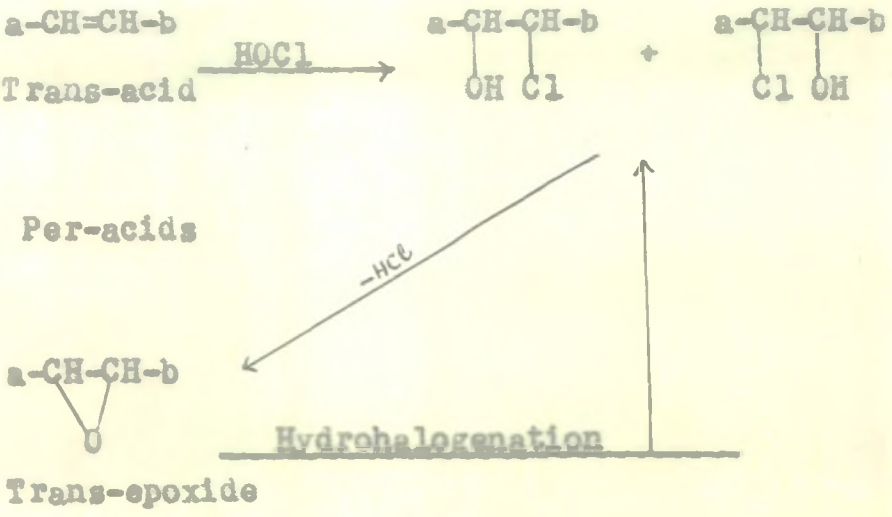
yield of 6(7):7(6)-chlorohydroxystearic acids melting at 47-52°. The product on repeated crystallisations yielded a pure mixture of 6(7):7(6)-chlorohydroxystearic acids m.p.55-56°. These are stereoisomeric with those prepared from the petroselinic acid or its epoxide.

The same 6(7):7(6)-chlorohydroxystearic acids m.p.55-56° were obtained when petroselaidic acid was treated with chlorine water.

The treatment of these chlorohydroxy acids with alkali resulted in the formation, in quantitative yields, of the trans-petroselaidic epoxide m.p.66-67°.

The hydrohalogenation of the petroselaidic acid epoxide thus formed, readily yielded 6(7):7(6)-chlorohydroxystearic acids identical with those obtained either by the action of hypochlorous acid solution or of chlorine water on petroselaidic acid.

The results are summarised below:



Preparation of the 6:7-Dihydroxystearic acids.

The low and high melting 6:7-dihydroxystearic acids, (threo-isomer, m.p.115-116° and erythro-isomer, m.p.122°) were prepared in good yields from petroselinic and petroselaidic acids respectively through the use of performic acid (cf. Swern)[57].

Conversion of erythro-6:7-dihydroxystearic acid m.p.122° into threo-isomer, m.p.115-116°.

6:7-dihydroxystearic acid m.p.122° was converted primarily to a cis-epoxide m.p.59-60° by the action of dry hydrogen chloride gas and the subsequent hot saponification of the viscous oily product. A small quantity of the low melting 6:7-dihydroxystearic acid m.p.115-116° was also obtained from the hydrolysed product. This indicated the possibility of progressive hydrolysis of the epoxide formed as a main product by the action of alkali.

The cis-epoxy acid m.p.59-60° on saponification either in a sealed tube at 170° or on simple refluxing, readily yielded the threo-6:7-dihydroxystearic acid m.p.115-116°.

On acid hydrolysis of the epoxide a solid was obtained which after crystallisation yielded low melting 6:7-dihydroxystearic acid m.p.115-116°.

The melting point was not depressed when a mixed melt was taken with the acid prepared by the oxidation of petroselaidic acid with alkaline potassium permanganate. The course of the above reactions may be represented as under:

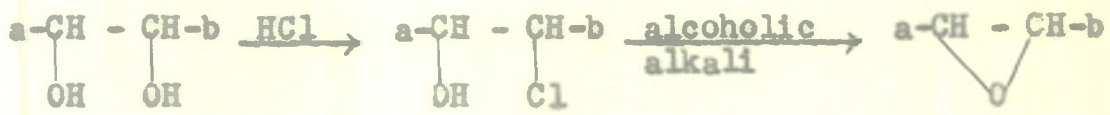
6:7-dihydroxystearic acid m.p.122° —HCl gas→ Chlorohydrins —alcoholic alkali→

6:7-epoxystearic acid m.p.59-60° —Hydrolysis→ 6:7-dihydroxystearic acid m.p.115-116°

Conversion of three-6:7-dihydroxystearic acid m.p.115-16° to erythro-isomer m.p.122°.

Under conditions similar to those described above the low melting 6:7-dihydroxystearic acid m.p.115-116° on treatment with dry hydrogen chloride gas afforded a viscous oil which on saponification yielded the trans-epoxide m.p.66-67°.

This epoxide on hydrolysis gave the high melting 6:7-dihydroxystearic acid m.p.122°.



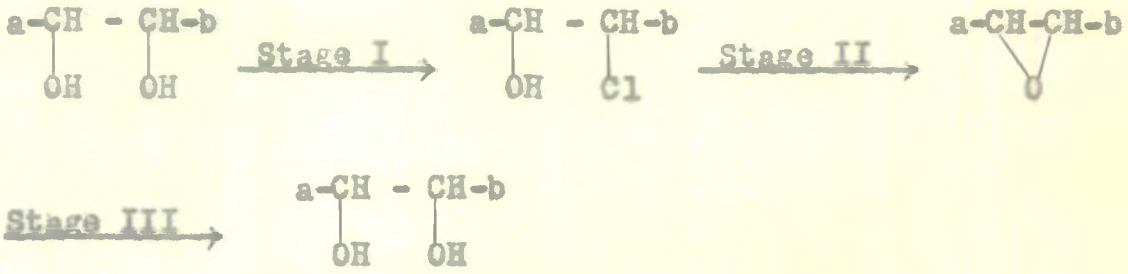
m.p. 115-116°

m.p.122°

These interconversions of the dihydroxystearic acids of 6:7-octadecenoic acid are in line with the earlier findings of King and Hilditch on the isomeric 9:10-dihydroxystearic acids obtained from oleic and elaidic acids. These authors have formulated the stereo-Chemical course of the transformations on assumptions which differ from each other in some fundamental respects. Their experimental evidence was based on almost similar findings in the interconversions of isomeric 9:10-hydroxy-stearic acids as under:

9:10-dihydroxy-stearic acid m.p.132° $\xrightarrow[\text{gas}]{HCl}$ Chloro-hydrins $\xrightarrow[NaOH]{dil}$ Oxido-stearic acid

$\xrightarrow{\text{Conc. NaOH}}$ 9:10-dihydroxystearic acid, m.p.95°



King concluding that the inversion occurs only during the opening of the epoxide ring (stage III), while Hilditch and Atherton on the other hand suggesting that the inversion takes place during the replacement of hydroxyl group by the chlorine atom (stage I). These latter authors at the same time assumed that the closure and the opening of the epoxy ring (stage II and III) takes place without inversion.

These results about the mutual transformations of the isomeric 6:7-dihydroxystearic acids m.p.115-116° and

m.p.122° show that the inversions of configurations occur in all the three stages as under:

(i) during the replacement of the hydroxyl group by chlorine atom

(ii) at the time of the closing of the epoxy ring and,

(iii) at the time of the opening of the epoxy ring.

King, from his work on the stereochemistry of the halogenohydroxystearic acids from oleic and elaidic acids, has already suggested this 3-stage inversion. This also supports Swern's assumption of the three fold inversions made on theoretical grounds.

6(7):7(6)-Bromohydroxystearic acids from petroselinic acid and its epoxide.

A 25-35% yield of a mixture of pure 6(7):7(6)-bromohydroxystearic acids m.p.36-37° was readily obtained when a solution of petroselinic acid was treated with sodium hypobromite solution in presence of an alkali. These acids were easily crystallisable from n-hexane or a mixture of low boiling petrol and benzene.

When the mixture of the bromohydroxystearic acids was treated with a dilute aqueous solution of an alkali, petroselinic epoxide m.p.59-60° was obtained.

The action of aqueous hypobromous acid on petroselinic acid in ether gave an oil which finally crystallised yielding 6(7):7(6)-bromohydroxystearic acids m.p. 36-37°. These acids were the same as those obtained by the action of sodium hydrobromite on petroselinic acid. On saponification with aqueous alkali these acids gave petroselinic epoxide m.p.59-60°.

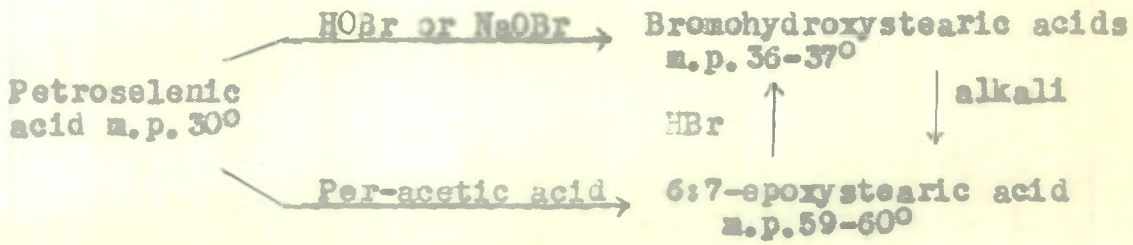
The treatment of the epoxide with hydrobromic acid yielded a product which on repeated crystallisations gave 6(7):7(6)-bromohydroxystearic acid m.p.36-37° (in good yields). The action of dilute alkali on these acids regenerated the original epoxide.

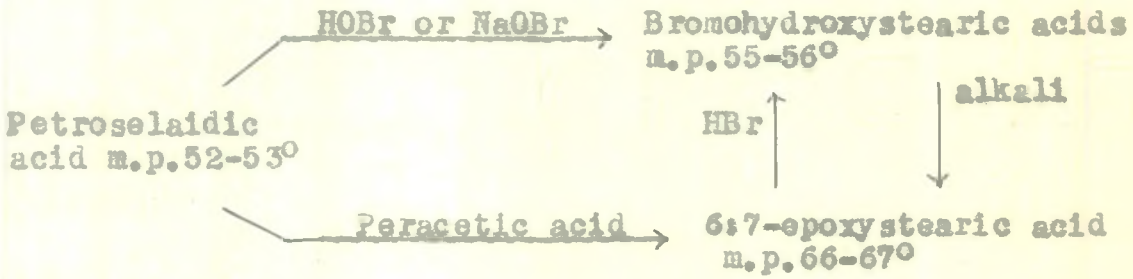
6(7):7(6)-Bromohydroxystearic acids from petroselaidic acid and its epoxide.

Petroselaidic acid on hypobromination with sodium hypobromite gave crystalline 6(7):7(6)-bromohydroxystearic acids m.p.55-56°. The action of hyporbomous acid on petroselaidic acid also reproduced the same acids. These bromohydroxy acids readily hydrolysed to trans-6:7-epoxystearic acid m.p.66-67°. The epoxy-acid on treatment with hydrobromic acid readily gave 6(7):7(6)-bromohydroxystearic acids m.p.55-56°.

The identity of these acids with the ones obtained on hypobromination of petroselaidic acid was established by a mix melt and a regeneration of the same epoxide on dehydrohalogenation of either mixture of acids.

The results of the hypobromination are summarised below:





6(7):7(6)-Iodohydroxystearic acids from petroselinic acid and its epoxide.

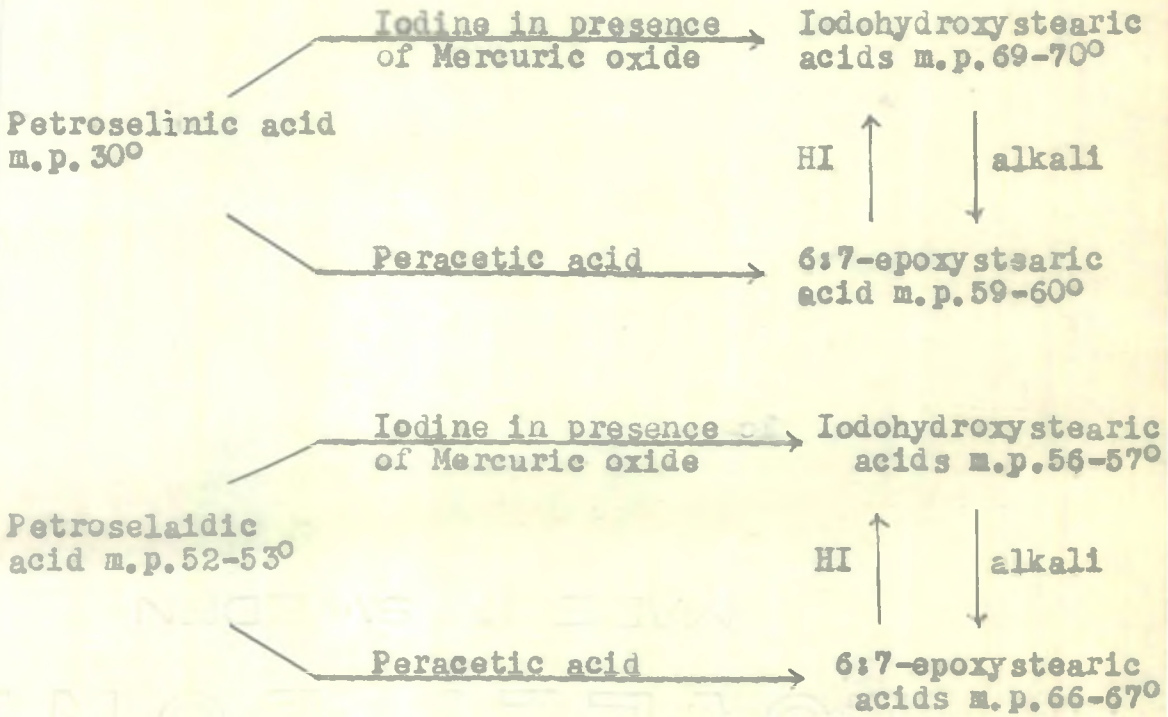
Petroselinic acid in moist ether reacted with iodine in presence of mercuric oxide to yield the corresponding 6(7):7(6)-iodohydroxystearic acids m.p.69-70°. These acids when treated with cold aqueous alkali furnished the petroselenic acid epoxide m.p.59-60°.

The same 6(7):7(6)-iodohydroxystearic acids were conveniently prepared by the action of hydroiodic acid on petroselinic acid epoxide m.p.59-60°. The latter was regenerated by the treatment of the 6(7):7(6)-iodohydroxystearic acids with cold alkali.

6(7):7(6)-Iodohydroxystearic acids from petroselaidic acid and its epoxide.

Under conditions similar to those described above a pure mixture of 6(7):7(6)-iodohydroxystearic acids m.p.56-57° was obtained both by the action of iodine in presence of mercuric oxide on petroselaidic acid and by the action of hydroiodic acid on petroselaidic acid epoxide. These acids in each case yielded the same epoxy acids on hydrolysis.

The following diagram gives all these reactions at a glance.



The foregoing results on bromo- and iodo-hydrins which are exactly the same in details as in the case of chlorohydrins lend further support to the earlier observation of the changes of configuration during hypohalogenation, hydrohalogenation and dehydrohalogenation of 6:7-octadecenoic acids and their epoxides respectively.

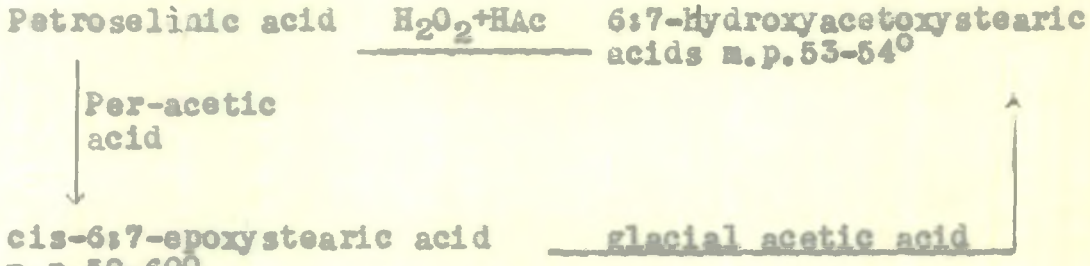
6(7):7(6)-Hydroxyacetoxystearic acids from petroselinic and petroselaidic acids.

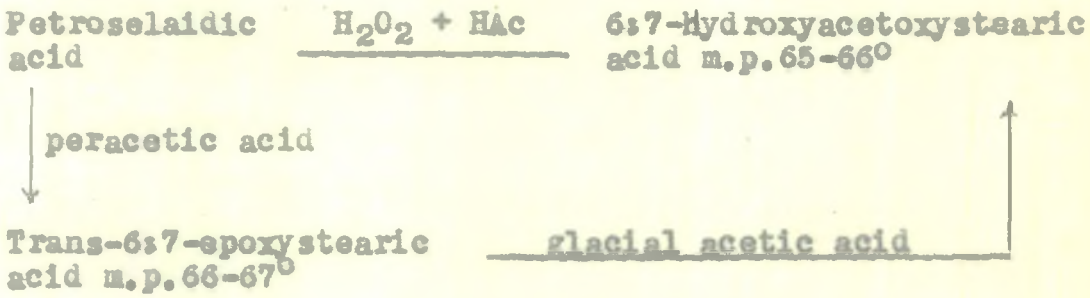
6(7):7(6)-Hydroxyacetoxystearic acids were prepared in two different ways (i) by the action of hydrogen peroxide on petroselinic acid in acetic acid medium; and (b) by the action of glacial acetic acid on petroselinic acid epoxide.

Both the procedures readily yielded a mixture of monoacetyl derivatives m.p.53-54° of the 6:7-dihydroxy-stearic acid m.p.115-116°. The hydroxyacetates obtained from two different sources were found to be identical on the basis of their mixed melting point. It has been found that the hydroxyacetoxy derivatives could only be obtained if the duration of reaction is reduced from that reported by King[58] in his studies on the oxidation of oleic and elaidic acids. A longer reaction time resulted only in the formation of 6:7-dihydroxystearic acid m.p.115-16°.

The oxidation of petroselaidic acid with hydrogen peroxide or of its epoxide with glacial acetic acid under conditions similar to those mentioned above, yielded the 6(7):7(6)-hydroxyacetoxystearic acids m.p.65-66°. The

results are summarised below:





The fact that the epoxy acids united readily with acetic acid to give the 6(7):7(6)-hydroxyacetoxystearic acids, suggested that these compounds are intermediates in the conversions of the epoxides to the corresponding dihydroxystearic acids. It is, however, difficult to find appropriate reaction conditions (particularly the time factor and the raction temperature) which will be

specific for the preparation of these compounds from mono-unsaturated acids. However, the present results indicate that most probably the following course of reactions, as suggested by Boeseken and Elsen[59], takes place during hydrogen peroxide oxidation.

R-CH(OAc)-CH(OH)-R´ and R-CH(OH)-CH(OAc)-R´

R-CH(OH)-CH(OH)-R´

CONCLUSIONS

C O N C L U S I O N S

The following conclusions can be drawn from the work described in this thesis.

(1) The hypochlorination of petroselinic acid either with a solution of sodium hypochlorite or chlorine water yields a mixture of 6(7):7(6)-chlorohydroxystearic acids m.p.59-60°.

(2) The direct hydrohalogenation of cis-6:7-epoxystearic acid (petroselinic acid epoxide) readily affords a mixture of 6(7):7(6)-chlorohydroxystearic acids, m.p. 59-60°, identical with the ones obtained by the hypochlorination of petroselinic acid.

(3) The identity of the chlorohydrins obtained from two different routes leads to the conclusion that the opening of the epoxide ring on hydrohalogenation is accompanied by an inversion in the configuration.

(4) The dehydrohalogenation of 6(7):7(6)-chlorohydroxystearic acids (obtained either by hypohalogenation of the acid or hydrohalogenation of the epoxide) gave the same cis-6:7-epoxystearic acid, m.p.59-60°.

(5) The fact that the epoxy acids from the two sources are identical leads to suggest that the change in the configuration occurs during the closing of the epoxide ring through dehydrohalogenation.

(6) That trans-petroselaidic acid on hypochlorination by either with hypochlorous acid or chlorine water yields a mixture of 6(7):7(6)-chlorohydroxystearic acids m.p.55-56°. These chlorohydrins behave in an analogous manner to those from petroselinic acid.

(7) Erythro-6:7-dihydroxystearic acid, m.p.122° and its threo-isomer m.p.115-116° have been successfully converted into each other through hydrohalogenation and subsequent dehydrohalogenation followed by hydrolysis.

(8) The above interconversions lead to the conclusion that the change in configuration also occurs during the replacement of one of the hydroxyl groups by a chlorine atom.

(9) That 6(7):7(6)-bromohydroxystearic acids, m.p. 36-37° are obtained both by hypobromination of petroselinic acid and by the hydrobromination of petroselinic acid

epoxide. The bromohydrins obtained by both the routes on dehydrohalogenation yield the same petroselinic acid epoxide.

(10) The hypobromination of petroselaidic acid or the hydrobromination of its epoxide gives the same mixture of 6(7):7(6)-bromohydroxystearic acids, m.p.55-56°.

(11) Petroselinic acid and its epoxide on treatment with hypoiodous acid and hydroiodic acid respectively yield the same 6(7):7(6)-iodohydroxystearic acids, m.p. 69-70°. These on dehydrohalogenation give the original epoxide.

(12) 6(7):7(6)-Iodohydroxystearic acids, m.p.56-57° were readily isolable by hypohalogenation and hydrohalogenation of petroselaidic acid and its epoxide respectively. The acids on treatment with alkali regenerate the original epoxide.

(13) The analogous behaviour of bromohydrins and iodohydrins confirm the earlier observations of the changes in configuration (three fold inversions) as described in the case of chlorohydrins.

(14) Hydrogen peroxide hydroxylation of petroselinic and petroselaidic acids in glacial acetic acid yielded the monoacetyl derivatives, 6(7):7(6)-hydroxyacetoxystearic acids m.p.53-54° amd m.p.65-66° respectively.

(15) These 6(7):7(6)-hydroxyacetoxystearic acids, m.p.53-54° and m.p.65-66° have also been obtained by the action of glacial acetic acid on the epoxides of petroselinic amkd and petroselaidic acids respectively.

(16) The fact that the hydroxyacetoxystearic acids are readily isolable from the product formed by the action of acetic acid on the epoxides suggests that these compounds are the intermediates in the conversion of the epoxides to the corresponding glycols (dihydroxy acids).

(17) The work on Anethum trifoliatum confirms all the findings already arrived at on the seed fats of the members of the family umbelliferae, and the fatty acid composition has been found to be palmitic 9.37%, petroselinic 48.85%, oleic 33.90% and linoleic acid 7.88%.

EXPERIMENTAL

Preparation of petroselinic acid.

The solid fatty acids from the seed oil of Anethum trifoliatum were purified by the lithium-salt-crystallisation method following the procedure of van Loon[45]. The liberated acids obtained from the recyrstallised lithium salts were converted into the methyl esters and fractionally distilled under reduced pressure. The main fraction was collected which on saponification yielded pure petroselinic acid m.p.30°(I.V. 89.4 ; acid value, 197.8).

Preparation of Petroselaidic acid.

The procedure of Lumb and Smith[60] was followed for the isomerisation of petroselinic acid with nitrous acid. The product thus obtained, on crystallisation twice from acetone, gave colourless shining crystals (yield 47%) of pure petroselaidic acid, m.p.52-53° (I.V. 89; acid value 198.0).

Performic acid hydroxylation of petroselinic and petroselaidic acids.

To a solution of pure petroselinic acid (20 g.) in 60 cc of formic acid at 25°, was added 25% hydrogen peroxide (9 g.) and oxidation was carried according to

the procedure of Swern and collaborators[57]. The crude oxidised product finally obtained was washed with light petroleum ether to remove the non-hydroxy acids. On crystallisation twice from ethanol, 10 g. of threo-6:7-dihydroxystearic acid, m.p.115-116° was obtained in the form of colourless shining needles.

Petroselaidic acid (16 g.), when oxidised with performic acid in the manner described above, gave a product which on recrystallisation from ethyl acetate afforded erythro-6:7-dihydroxystearic acid (7.5 g) m.p.122°. The identity of the threo- and the erythro-hydroxy acids was confirmed by a mixed melt with an authentic sample.

Epoxidation of petroselinic and petroselaidic acids with per-acetic acid.

Petroselinic acid (15 g.) was mixed with 64 cc. of a solution of peracetic acid and the oxidation was continued for four hours at 20° according to the procedure of Swern et al[27]. The solid product was first crystallised from aqueous alcohol to give the crude epoxide (11.5 g.). The product thus obtained, on recrystallisation from acetone, gave a crystalline solid (cis-6:7-epoxystearic acid) which melted sharply at 59-60°.

Petroselaidic acid (10 g.) when treated with peracetic acid as in the above case, gave trans-6:7-epoxystearic acid (6.5 g.) m.p.66-67°.

The identity of the above epoxides was established by a mixed melting point determination with authentic samples.

6(7):7(6)-Chlorohydroxystearic acids from petroselinic acid.

(a) These acids were prepared (cf. King)[40] by dissolving petroselinic acid (8 g.) in water (800 cc) containing potassium hydroxide (1. 8 g.) and adding slowly, with constant shaking, a solution of sodium hypochlorite (120 cc., prepared by passing chlorine gas into a saturated aqueous solution of sodium bicarbonate). Carbon dioxide was passed into the solution till saturation and the solution was kept overnight. The resulting solution was acidified with dilute sulphuric acid solution and the excess hypochlorous acid was destroyed by sodium sulphite. On extraction with ether a semi-solid product(I.V. 6.5) was obtained which on crystallisation from n-hexane yielded the crude chlorohydroxystearic acids (4.8 g.) m.p.50-55°. The product was

purified by crystallisation from a mixture of light petrol and benzene. The final recrystallisation from methyl alcohol gave a mixture of pure 6(7):7(6)-chlorohydroxystearic acids in colourless crystalline form, m.p.59-60°. (Equiv., 334).

Analysis; Found: C, 64.38; H, 10.17; Cl, 10.41%
required for $C_{18}H_{35}O_3Cl$:
C, 64.5; H, 10.3; Cl, 10.8%.

The mother liquors obtained during recrystallisation were collected. On removal of the solvent a viscous oil was obtained which did not solidify on keeping for two weeks. Attempts to crystallise the oil failed to produce any solid substance.

(b) Petroselinic acid (5 g.) was suspended in 60 cc. of water to which was added slowly, with constant shaking, a moderately concentrated solution of freshly prepared chlorine water till a smell of chlorine persisted and the solution was shaken mechanically for about an hour. The reaction product was isolated as above by extraction with ether. It crystallised with difficulty from n-hexane at 0° after two days and a solid (0.8 g.) was obtained which melted at 47-54°. The pure chloro-

hydroxystearic acids m.p.59-59.5° were obtained by repeated crystallisation from methyl alcohol. The product showed no depression on a mixed melt with the acids prepared above.

Dehydrohalogenation of the 6(7):7(6)-chlorohydroxystearic acids, m.p.59-60°.

The 6(7):7(6)-chlorohydroxystearic acids (1 g.) were dissolved in 50 cc. solution of sodium hydroxide (0.2 g.) and the resulting solution was allowed to stand for four hours. The solid product (0.85 g.), obtained on acidification of the solution with dilute sulphuric acid, was crystallised twice from acetone and yielded 6:7-epoxy-stearic acid in the form of colourless shining crystals, m.p.59-60°. It showed no depression in melting point on admixture with the epoxy acids prepared from petroselinic acid by peracetic acid oxidation.

6(7):7(6)-Chlorohydroxystearic acids from cis-6:7-epoxystearic acid.

cis-6:7-epoxystearic acid (petroselinic acid epoxide) m.p.59-60° (4 g.) dissolved in ether (40 cc.) was treated with 10N-hydrochloric acid (2.6 cc.) and the

mixture was mechanically shaken for about an hour (cf. King). The solution after being freed from mineral acid was dried and evaporation of the solvent yielded a solid residue of 6(7):7(6)-chlorohydroxystearic acids which crystallised from light petroleum ether-benzene mixture in colourless cyrstalline product (3.8 g.) m.p.59-60° (Equiv. 335). It showed a depression in mixed m.p. with the original epoxide but on the ether hand no depression was observed with the 6(7):7(6)-chlorohydroxystearic acids prepared from petroselinic acid-

The 6(7):7(6)-chlorohydroxystearic acids on treatment with 0.1N-sodium hydroxide solution for two hours at room temperature gave almost a theoretical yield of the original epoxy acid.

6(7):7(6)-Chlorohydroxystearic acids from petroselaidic acid.

(a) A solution of petroselaidic acid (5 g.) in water (500 cc.) containing potassium hydroxide (1.12 g.) was treated with a solution of sodium hypochlorite (75 cc) in the manner described earlier. The ether extraction of the reaction product yielded a semi-solid sticky mass

(I.V. 8) which on crystallisation from n-hexane afforded a mixture of crude 6(7):7(6)-chlorohydroxystearic acids (3.4 g.) m.p.47-52°. The product on recrystallisation first from a mixture of light petrol and benzene and finally from methyl alcohol yielded a colourless crystalline mixture of pure 6(7):7(6)-chlorohydroxystearic acids m.p.55-56° (Equiv. 333.5).

Analysis; Found: Cl, 10.53% required for $C_{18}H_{35}O_3Cl$, Cl, 10.8%.

(b) A suspension of petroselaidic acid (4 g.) in 50 cc of water was allowed to react with chlorine water under conditions employed in the case of petroselinic acid. A semi-solid product was isolated which on repeated crystallisations from n-hexane afforded a mixture of pure 6(7):7(6)-chlorohydroxystearic acids (Equiv.334) m.p. and mixed melting point 55-56° with the ones obtained by using sodium hypochlorite solution.

These acids on saponification with cold aqueous-alkali for four hours yielded a product which was crystallised twice from acetone in the form of a colourless

crystalline substance sharply melting at 66-67°. It was identified to be the trans-6:7-epoxystearic acid (petroselaidic acid epoxide) by a mixed melting point determination with an authentic sample.

6(7):7(6)-Chlorohydroxystearic acids from trans-6:7-epoxystearic acid.

A solution of the petroselaidic acid epoxide m.p.66-67° (3 g.) in ether (300 cc.) was shaken vigorously with 10N-hydrochloric acid (2 cc.) for 1 hour. The solid product recovered in the usual manner, on crystallisation first from n-hexane and then from light petrol-benzene mixture gave a colourless crystalline substance m.p.55-56°. It was found by a mixed melt to be the pure 6(7):7(6)-chlorohydroxystearic acids of petroselaidic acid.

The saponification of the above product with cold alkali regenerated the trans-6:7-epoxystearic acid m.p. 66-67° (unchanged when mixed with the original epoxy acid).

Interconversion of the isomeric 6:7-dihydroxystearic acids.

The mutual transformations of the isomeric 6:7-dihydroxystearic acids (threo-isomer m.p.115-116° and

erythro-isomer m.p.122°, prepared earlier) were carried out according to King's[58] procedure.

Conversion of erythro-6:7-dihydroxystearic acid m.p.122° into its threo-isomer m.p.115-116°.

The erythro-isomer m.p.122° (3 g.) was heated for four hours at 160° in a current of dry hydrogen chloride gas. The product obtained was a dark brown viscous oil which was refluxed with excess of 2N-potassium hydroxide for two hours. The reaction product was dissolved in water (500 cc.) and subsequently acidified with cold dilute sulphuric acid. A solid product was obtained which was washed and dried under vacuum. On fractional crystallisation from low boiling petroleum ether, a crystalline solid (0.5 g.) melting at 112-113° was obtained. A single crystallisation from ethanol raised the melting point to 115-116°. It showed no depression on mixed melt with a genuine sample of threo-6:7-dihydroxystearic acid.

The second fraction (1.44 g.) crystallised from methyl alcohol in a colourless crystalline form m.p.59-60°. It was found to be the cis-6:7-epoxystearic acid by a comparision and the mixed melting point determination with an authentic sample. The epoxy acid on

hydrolysis with caustic potash or with dilute sulphuric acid afforded a good yield of the threo-6:7-dihydroxy-stearic acid m.p. and mixed m.p.115-116° with the dihydroxystearic acid prepared by the oxidation of petroselaidic acid with alkaline potassium permanganate.

Hydrolysis of the epoxy acid with 7N-potassium hydroxide at 170° also results in the formation of the same compound.

Conversion of threo-6:7-dihydroxystearic acid m.p.115-16° into its erythro-isomer m.p.122°.

The threo-isomer (4 g.), m.p.115-116° was treated with dry hydrogen chloride gas in the same way as above. On saponification of the viscous oil, the trans-6:7-epoxystearic acid (1.8 g.) m.p.66-67° was obtained which showed no depression when a mixed m.p. was taken with the epoxy acid prepared by the action of peracetic acid on petroselaidic acid.

The hot saponification of the epoxy acid with the alkali yielded the corresponding 6:7-dihydroxystearic acid (erythro-isomer), which was crystallised from ethyl acetate in a colourless shining form, m.p.122°, alone or

when admixed with the sample obtained by the performic acid hydroxylation of petroselaidic acid.

6(7):7(6)-Bromohydroxystearic acids from petroselinic acid.

(a) A solution of sodium hypobromite (90 cc, prepared from bromine and aqueous sodium carbonate) was gradually added with constant shaking to a solution of petroselinic acid (4 g.) in 0.1N-potassium hydroxide (160 cc.) till a persistant light brown-coloured solution was obtained. After 30 minutes the ether extraction of the reaction product (cf. King) yielded an oil which was taken up in light petroleum ether and the solution was kept in a refrigerator.

After two days a solid product (1 g.) was obtained which on recrystallisation from n-hexane furnished pure 6(7):7(6)-bromohydroxystearic acids as a colourless crystalline product, m.p. 36-37°.

Analysis; Found: C, 56.06; H, 8.55; Br, 21.62%

required for $C_{18}H_{35}O_3Br$

C, 56.94; H, 9.23; Br, 21.10%.

Addition of a solution of hypobromous acid (10 cc prepared by bromine and freshly precipitated mercuric oxide, Cf.King) to a cooled solution of petroselinic acid (3 g.) in ether (30 cc) gave an oil as the reaction product. The oil was dissolved in light petroleum ether and kept for two days at 0°. A solid product (0.6 g.) thus obtained, on crystallisation from a mixture of light petrol and benzene yielded the 6(7):7(6)-bromohydroxystearic acids m.p.36-37°, alone or when admixed with the preceding sample.

The 6(7):7(6)-bromohydroxystearic acids on saponification with 2 N-sodium hydroxide solution for one hour at room temperature afforded a good yield of the cis-6:7-epoxystearic acid m.p.59-60°. Its identity was established by a mixed melt with an authentic sample.

(b) 6(7):7(6)-Bromohydroxystearic acids from cis-6:7-epoxystearic acid.

Petroselinic acid epoxide (2 g.) m.p.59-60° in ether (20 cc) was treated (cf.King)[58] with Hydrobromic acid (2 cc). The reaction product (2.4 g.) on crystallisation from n-hexane yielded 6(7):7(6)-bromohydroxystearic acids in a colourless crystalline form, m.p.36-37°. The melting point was not depressed by admixture with a specimen of 6'7):7(6)-bromohydroxystearic acids prepared earlier.

These acids on treatment with alkali furnished the original epoxy acid m.p. and mixed m.p.59-59.5°.

6(7):7(6)-Bromohydroxystearic acids from petroselaidic acid.

Petroselaidic acid (5 g.) was treated with sodium hypobromite solution (100 cc. freshly prepared) as described earlier. The reaction product finally yielded a pure mixture of 6(7):7(6)-bromohydroxystearic acids (1.4 g.) as a colourless crystalline solid sharply melting at 55-56°.

Analysis; Found: Br, 20.56% required for $C_{18}H_{35}O_3Br$, Br, 21.1 %.

A solution of petroselaidic acid (2 g.) in ether (20 cc.) was reacted with a freshly prepared solution of hypobromous acid and the product was worked up in essentially the same way as described earlier. This on crystallisation from n-hexane gave 6(7):7(6)-bromohydroxystearic acids m.p.55-56° alone or when admixed with the sample obtained earlier.

These acids on treatment with aqueous alkali readily yielded an epoxy acid m.p.65-66°, identified as trans-6:7-epoxystearic acid.

6(7):7(6)-Bromohydroxystearic acids from trans-6:7-epoxystearic acid.

Petroselaidic acid epoxide m.p.66-67° (2 g.) when treated with hydrobromic acid as described earlier yielded a product which could be easily crystallised from a mixture of light petrol and benzene to give the 6(7):7(6)-bromohydroxystearic acids m.p. 54.5-55.5°. A mixture of the two samples of 6(7):7(6)-bromohydroxystearic acids in equal quantities melted at 54-56°.

On saponification with the alcoholic potassium hydroxide the original epoxy acid was obtained which showed no depression when a mixed melting point was taken with an authentic sample of trans-6:7-epoxystearic acid.

6(7):7(6)-Iodohydroxystearic acids from petroselinic acid.

Petroselinic acid (5 g.) was dissolved in moist ether (30 cc.) containing a suspension of mercuric oxide (2.05 g.; freshly precipitated). Finely powdered iodine (4.5 g.) was then gradually added with constant shaking and the mixture was again mechanically shaken for 15 minutes. Theethereal solution was filtered and the filtrate was washed thoroughly with a dilute solution of sodium sulphite and then with water. Mercury was removed

as sulphide by treatment with hydrogen sulphide gas. The residual oil thus obtained (cf. King)[40] was dissolved in petroleum ether, b.p. 40-60° (80 cc.). On cooling for two days at 0° a crude deposit of a mixture of 6(7):7(6)-iodohydroxystearic acids m.p.62-67° (2.1 g.) was obtained. This on subsequent recrystallisation from n-hexane furnished the pure 6(7):7(6)-iodohydroxystearic acids as a colourless product melting sharply at 69-70°.

Analysis: Found; C, 50.79; H, 8.63; I, 29.26%
required for $C_{18}H_{35}O_3I$
C, 50.7 ; H, 8.3 ; I, 29.8 %.

The 6(7):7(6)-iodohydroxystearic acids on treatment with cold 0.1N-caustic soda solution for half an hour gave a good yield of cis-6:7-epoxystearic acid m.p.59-60°.

<u>6(7):7(6)-Iodohydroxystearic acids from cis-6:7-epoxystearic acid.</u>

A solution of petroselinic acid epoxide (2 g.) m.p.59-60° in ether (20 cc.) was treated with hydroiodic acid (2 cc.) and the solution was allowed to stand for one hour, shaking at times. After removal of the solvent

the residue (2.6 g.) was taken up in n-hexane and kept in the refrigerator. The solid thus obtained on recrystallisation gave pure 6(7):7(6)-iodohydroxystearic acids as a colourless product, m.p. 69-69.5°, alone or when admixed with the sample obtained earlier.

Treatment of these acids with alkali regenerated the original epoxy acid m.p. and mixed m.p. 59-60°.

6(7):7(6)-Iodohydroxystearic acids from petroselaidic acid.

A solution of petroselaidic acid (4 g.) in moist ether (25 cc) was treated with iodine (3.6 g.) and mercuric oxide (1.6 g.) in essentially the same way as described earlier. The solid (1.75 g.) recovered from n-ehxane was successively recrystallised from methanol. Finally a pure mixture of iodohydroxystearic acids m.p. 56-57° was obtained.

Analysis: Found; I, 29.45% required for $C_{18}H_{35}O_3I$ I, 29.8 %.

The 6(7):7(6)-iodohydroxystearic acids on treatment with 0.1N-caustic soda solution afforded the trans-6:7-epoxystearic acid m.p. 65-67°. This melting point was not depressed by admixture with an authentic sample.

6(7):7(6)-Iodohydroxystearic acids from trans-6:7-epoxystearic acid.

Petroselaidic acid epoxide (2 g.) m.p.66-67° in ether (20 cc) was allowed to react with hydroiodic acid (2 cc.) under conditions similar to those described earlier. The recovered crude product, crystallised from n-hexane, had a m.p.55-56.5°. Its identity as pure 6(7):7(6)-iodohydroxystearic acids was established by a mixed melt with a sample obtained above.

The dehydrohalogenation of these acids with alkali reproduced the same epoxy acid m.p.65-66°.

6(7):7(6)-Hydroxyacetoxystearic acids from petroselinic acid and its epoxide.

(a) Hydrogen peroxide (100 vol, 4 cc.) was added to a solution of petroselinic acid (5 g.) in glacial acetic acid (100 cc.). The mixture was kept at room temperature (20°C) for 7 days and then for 2 days at 0° after addition of water (cf. King)[ ]. The solid thus obtained was filtered, washed free of acetic acid and dried in a desiccator. The dried sticky product was taken up in warm benzene and the dihydroxystearic acid

was filtered off. On keeping the benzene solution at 0° for 24 hours a crude deposit of 6:7-hydroxyacetoxystearic acids (2.5 g.) was obtained which on recrystallisation twice from acetone yielded the pure acids in a colourless crystalline form m.p.53-54° (Equiv. 354; Calc.Equiv.358).

The benzene insoluble portion of the crude oxidised product on crystallisation from acetone yielded threo-6:7-dihydroxystearic acid (0.5 g.) m.p. and mixed m.p.115-116°.

When the duration of the above reaction was extended to 12 days (cf. King) the oxidised product in the present case was found to be mainly consisting of dihydroxy compound.

The 6(7):7(6)-hydroxyacetoxystearic acids were readily saponifiable by 2N-caustic soda solution and afforded a good yield of threo-6:7-dihydroxystearic acid m.p.115-116°, alone or when admixed with an authentic sample.

(b). Action of acetic acid on cis-6:7-epoxystearic acid.

A solution of petroselinic acid epoxide m.p.59-60° (2 g.) in glacial acetic acid (50 cc) was kept for 7 days

at room temperature. Water was then added and the solution was kept in a refrigerator for 24 hours. The solid 6(7):7(6)-hydroxyacetoxystearic acids (1.3 g) were filtered and on crystallisation from acetone a pure sample of the acids in colourless form, m.p.53-53.5°, was obtained. The m.p. of the latter was not depressed by admixture with a specimen of hydroxyacetoxystearic acids prepared from petroselinic acid.

Saponification of the above acids readily yielded the low melting threo-6:7-dihydroxystearic acid m.p. and mixed m.p.115-116°.

6(7):7(6)-Hydroxyacetoxystearic acids from petroselaidic acid and its epoxide.

(a). A solution of petroselaidic acid (4 g.) in glacial acetic acid (80 cc) was allowed to react with a solution of hydrogen peroxide (100 vol., 3.5 cc.) for a period of 7 days as described earlier. Finally a solid product (2.2 g.) was obtained which on subsequent recrystallisation furnished 6(7):7(6)-hydroxyacetoxystearic acids as colourless shining crystals having m.p.65-66° (Equiv., 356; Calc. Equiv., 358).

The benzene insoluble portion (0.4 g.) on crystallisation from ethyl acetate yielded the high melting erythro-6:7-dihydroxystearic acid m.p. and mixed m.p.122°.

On saponification with 2N-caustic soda solution the hydroxyacetoxystearic acids gave erythro-6:7-dihydroxystearic acid m.p.121-122° alone or mixed with an authentic sample.

(b). Action of acetic acid on trans-6:7-epoxystearic acid.

Petroselaidic acid epoxide m.p.66-67° (2 g.) was dissolved in glacial acetic acid (50 cc) and the solution was allowed to stand for 7 days at room temperature. The product on working up as mentioned earlier yielded the 6(7):7(6)-hydroxyacetoxystearic acids (1.4 g.) in the form of a colourless crystalline product m.p.65-66° alone or when admixed with the preceding sample.

Alkali saponification of these acids readily afforded a good yield of erythro-6:7-dihydroxystearic acid m.p. and mixed m.p. with an authentic sample 122°.

Chemical Examination of The Seed-oil of Anethum trifoliatum.

The oil from Anethum trifoliatum was extracted with petroleum ether (b.p. 40-60°) from well powdered seeds obtained locally. The recovery of the solvent gave a greenish yellow oil which had the following characteristics:

TABLE I.

Fat content.	13.5 %
Sp. Gr. at 25°.	9.9112
Ref. Index at 25°.	1.4572
I.V. (Hanus).	91.4
Sap. Value.	159.2
Acid Value.	11.5
Unsaponifiable.	13.2 %

The resinous mass was removed by washing the ethereal solution of the oil with dilute aqueous sodium carbonate solution.

The oil was saponified with excess of alcoholic caustic potash and the unsaponifiable matter was removed by thoroughly exhausting the soap solution with ether. The decomposition of the soap solution gave crude mixed fatty acids which were separated into solid and liquid acids by Hilditch's modification of Twitchell's lead-salt-alcohol method.

The mixed fatty, solid and liquid acids have the following constants:

TABLE II.

	%	I.V.	S.V.
Mixed fatty acids.	82.2	92.3	199.5
Solid acids.	56.0	77.5	201.5
Liquid acids.	44.0	100.8	197.1

The liquid and solid acids were separately esterified with methanol in the usual manner and the esters fractionally distilled under reduced pressure (2 mm.). The percentages of the individual acids in each ester fraction, calculated from iodine value and saponification equivalent (S.E.) figures, in conjunction

with qualitative examination data of the fractions, is given in tables III, IV and V below:

T A B L E III.

Methyl esters of liquid acids.

Fraction	Wt/gm.	I.V.	S.E.	Estimated composition Palmitate.	Oleate	Linoleate.	Unsap.
L_1	4.5	83.0	281.2	0.72	3.22	0.56	-
L_2	3.9	85.2	290.1	0.54	2.87	0.49	-
L_3	4.2	98.9	291.3	-	3.58	0.62	-
L_4	4.5	103.2	293.6	-	3.62	0.88	-
L_5	5.3	106.6	294.5	-	4.05	1.25	-
L_6	4.1	100.9	299.3	-	2.96	0.93	0.21
	26.5			1.26	20.30	4.73	0.21
		% as esters		4.7	76.6	17.8	0.9
		% as acids		4.7	76.6	17.8	0.9

T A B L E IV.

Methyl esters of solid acids.

Fraction	Wt/gm	I.V.	S.E.	Estimated composition. Palmitate	Petroselinate
S_1	4.2	73.2	284.9	0.70	3.50
S_2	4.5	75.1	285.5	0.60	3.90
S_3	5.1	75.6	287.6	0.67	4.43
S_4	3.5	78.8	289.7	0.28	3.22
	17.3			2.25	15.05
			% as esters	13.0	87.0
			% as acids	13.0	87.0

TABLE V.

Estimated composition of Mixed fatty acids.

Acids.	'Solid' %	'Liquid' %	Total %	% excluding unsaponifiable.
Palmitic	7.28	2.07	9.35	9.37
Petroselinic	48.72	-	48.72	48.85
Oleic	-	33.75	33.75	33.90
Linoleic	-	7.79	7.79	7.88
Unsaponifiable	-	0.39	0.39	-

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Chemische Untersuchung des Samenfettes von Seseli indicum

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Es wurde gefunden, daß das fette Öl aus den Samen Seseli indicum W. & A. fettlösliche Cumarine enthält. Die Zusammensetzung der cumarinfreien Fettsäuren, die durch Esterfraktionierung bestimmt wurde, war: Harzsäuren 3 %, Palmitinsäure 6.18 %, Petroselinsäure 46.06 %, Ölsäure 30.96 % und Linolsäure 13.8 %.

Estudio químico de la grasa de semillas del Seseli indicum

Se ha encontrado que el aceite de las semillas de Seseli indicum W. & A. contiene cumarinas solubles en grasas. La composición de los ácidos grasos libres de cumarina, determinada por fraccionamiento de sus ésteres, es: ácidos resínicos 3 %, ácido palmítico 6.18 %, ácido petroselínico 46.06 %, ácido oleico 30.96 % y ácido linoleico 13.8 %.

Chemical Investigation of the Seed-fat of Seseli indicum

The fixed oil from the seeds of Seseli indicum, W. & A., has been found to contain fat-soluble coumarins. The composition of coumarin-free fatty acids, as determined by the ester-fractionation method was found to be resin acids 3.00 %, palmitic 6.18 %, petroselinic 46.06 %, oleic 30.96 % and linoleic acid 13.30 %.

Analyse chimique des corps gras de la graine de Seseli indicum

On a trouvé que l'huile grasse des graines de Seseli indicum W. & A., contient de la coumarine soluble dans les corps gras. La composition des acides gras ne contenant pas de coumarine, telle qu'elle a été déterminée par la methode de fractionnement des esters, est la suivante: acides resiniques 3 %, acide palmitique 6.18 %, acide petroselinique 46.06 %, acide oléique 30.96 % et acide linoléique 13.8 %.

Seseli indicum W. & A., gemeinhin als „Ajmod" bekannt, gehört zu der Familie der Umbelliferen. Die Samen werden benutzt als Mittel gegen Rundwürmer und als Stimulans, Blähungsmittel und zur Verdauungsförderung[1]. *E. Späth, P. K. Bose, J. Matzke* und *N. Ch. Guha*[2] haben die Anwesenheit von drei Cumarinen, Seselin, Bergapten und Isopimpinellin, festgestellt, die sie aus dem Petroläther-Extrakt der Samen isolierten. Das fette Öl scheint bisher nicht untersucht worden zu sein.

Im Verlauf unserer Untersuchungen wurde festgestellt, daß dieses Öl im Gegensatz zu anderen Samenfetten der Umbelliferen die besondere Eigenschaft besitzt, die fettlöslichen Cumarine festzuhalten. Es erwies sich als besonders schwierig, die Cumarine vollständig aus dem Öl zu entfernen. So wurde versucht, sie auf folgende Arten abzutrennen: Durch Abkühlen des Petroläther-Extraktes auf 0° C; durch Behandlung der Samen vor der Ölextraktion mit heißem Alkohol; durch Extrahieren der Samen unter Druck und durch Vakuum-Destillation des Fettsäure-Gemisches[3]. Diese Versuche zeigten jedoch keinen Erfolg. In allen Fällen waren noch kleine Mengen Cumarine im Öl enthalten; sie gingen mit den Methylestern bei deren Destillation über und sublimierten im Kondensor, wodurch der Prozeß unausführbar wurde.

Um diese Schwierigkeit zu überwinden, wurden die Cumarine soweit wie möglich dadurch abgetrennt, daß der Petroläther-Extrakt des Öles auf 0° abgekühlt wurde und danach die zurückgehaltenen Cumarine durch Behandlung des Fettsäure-Gemisches mit verdünnter wäßriger Natriumkarbonat-Lösung isoliert wurden[4]. Die Zusammensetzung der Fettsäuren wurde dann mit Hilfe der Esterfraktionierungs-Methode bestimmt. Die auf diese Weise erhaltenen Resultate stimmen im allgemeinen überein mit der Annahme, daß alle zu den Umbelliferen gehörenden Samenfette durch die Anwesenheit großer Mengen Glyceride des festen Isomers der Ölsäure (Petroselinsäure) charakterisiert sind.

Kürzlich haben *G. Kurono* und *T. Sakai*[5], die eine Anzahl Umbelliferen-Samenfette (japanische Varietäten) untersucht haben, über die Anwesenheit von Spuren Petroselaidinsäure in einigen dieser Öle berichtet, aber bei unserer Untersuchung (mit der üblichen Analysenmethode) konnte kein Hinweis auf die mögliche Anwesenheit dieser Säure gefunden werden.

Experimentelles

Die getrockneten und zerkleinerten Samen wurden mit Petroläther extrahiert (40—60° C), und der größte Teil der Cumarine dadurch entfernt, daß der Petroläther-Extrakt bei 0° C über Nacht stehengelassen wurde. Die so erhaltene feste Masse ergab zwei kristalline Produkte mit Schmelzpunkten von 120—122° C und 189—190° C, die als Seselin und Bergapten identifiziert wurden, wie bereits von *Späth* und Mitarbb. mitgeteilt[2]. Das Lösungsmittel wurde dann vollständig entfernt und ein dunkelgrünes Öl mit folgenden Kennzahlen erhalten:

Fett-Gehalt	20.0 %	VZ	148.6
Dichte bei 31° C	0.9011	JZ	82.1
$n\frac{D}{31}$	1.4360	Unverseifbares	18.5 %

Der große Gehalt an Unverseifbarem, den man stets bei Samenfetten von Umbelliferen findet, erklärt die niedrige Verseifungszahl des Öls[6].

Durch Erhitzen im Vakuum wurde das Öl von flüchtigen Bestandteilen befreit und dann mit alkoholischer Kalilauge verseift. Nach Entfernen des Unverseifbaren wurden aus der Seifenlösung durch Zersetzung die gemischten Fettsäuren erhalten (71.5 %).

Die zurückgehaltenen Cumarine wurden zur Trennung vom Fettsäure-Gemisch im Ätherüberschuß aufgenommen und die ätherische Lösung tropfenweise mit verdünntem wäßrigem Natriumkarbonat behandelt. Hierdurch wurden die Fettsäuren als Seifen niedergeschlagen, während die Cumarine im Äther zurückblieben. Der Prozeß wurde so lange wiederholt, bis das Fettsäure-Gemisch vollständig abgetrennt war. Die so erhaltenen Fettsäuren waren mit harzartigen Substanzen verunreinigt[7]. Die Harzsäuren wurden mit Hilfe der gravimetrischen Methode von *Twitchell* ermittelt und bildeten 3 % der Gesamtfettsäuren. Mit Hilfe der Bleisalz-Alkohol-Methode von *Twitchell* wurden daraufhin die Fettsäuren in ihre festen und flüssigen Komponenten getrennt. Auf diese Weise wurde gefunden, daß im ganzen 3 % Harzsäuren, 50.5 % feste Fettsäuren und 46.5 % flüssige Fettsäuren anwesend waren. Die 3 Gruppen Fettsubstanzen hatten folgende Kennzahlen:

	JZ	Verseifungsäquivalent
Gesamtfettsäuren	97.6	277.3
Feste Säuren	83.0	276.1
Flüssige Säuren	104.8	291.4

Der Anteil der individuellen Säureester innerhalb jeder Fraktion wurde auf Grund der Jodzahl berechnet unter Berücksichtigung des qualitativen Befundes. Die Bestimmung der Zusammensetzung der Fettsäuren auf Grund der Ester-Fraktionierung ist in Tabb. 1 und 2 wiedergegeben.

Tabelle 1

Methylester der festen Säuren

Fraktion	Gew. in g	Sdp. 3 mm	JZ	Verseifungsäquivalent	Ber. Zusammensetzung Gew. in g Palmitat	Petroselinat
S_1	2.61	bis 160° C	74.30	280.5	0.33	2.28
S_2	3.99	160—165° C	76.20	282.2	0.42	3.57
S_3	4.03	165—170° C	78.25	287.4	0.32	3.71
S_4	4.55	Rückstand	79.55	289.8	0.30	4.25
Insges.	15.18				1.37	13.81
			% Ester		9.02	90.98
			% Säuren		9.01	90.99

Tabelle 2

Methylester der flüssigen Säuren

Fraktion	Gew. in g	Sdp./3 mm	JZ	Verseifungsäquivalent	Ber. Zusammensetzung Gew. in g Palmitat	Oleat	Linoleat	Unv.
L_1	3.29	bis 170° C	100.5	279.6	0.44	2.34	0.51	—
L_2	3.49	170—171° C	113.0	290.3	0.09	2.31	1.09	—
L_3	4.22	171—172° C	115.8	295.4	—	2.73	1.49	—
L_4	4.38	Rückstand	100.0	305.9	—	2.83	1.55	0.1
Insges.	15.38				0.53	10.21	4.54	0.1
			% Ester		3.44	66.38	29.52	0.66
			% Säuren		3.42	66.40	29.52	0.66

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Identifizierung der Fettsäuren

Palmitin-, Petroselin-, Öl- und Linolsäure wurden in den Esterfraktionen folgendermaßen nachgewiesen:

Fraktionen:

S_1—S_4 Palmitinsäure, Schmp. 59—61° C
6,7-Dihydroxystearinsäure Schmp. 121—122° C

L_1—L_2 Palmitinsäure Schmp. 59—61° C
Dihydroxystearinsäure, Schmp. 130—132° C
Tetrahydroxystearinsäure, Schmp. 170—172° C.

Die Bromierung der aus den Estern erhaltenen flüssigen Säuren (L_3—L_4) ergab eine kristalline Tetrabromstearinsäure, Schmp. 113—114° C, die keine Schmelzpunkts-Depression ergab, wenn sie mit einer authentischen Probe von Tetrabromstearinsäure zusammen geschmolzen wurde. Es konnte kein ätherunlösliches Hexabromid isoliert werden, wodurch die Abwesenheit von Linolensäure in den flüssigen Fettsäuren bewiesen ist.

Isolierung und Elaidinierung von Petroselinsäure

Petroselinsäure wurde aus den festen Fettsäuren durch Kristallisation aus 95%igem Alkohol bei 0° C isoliert. Sie wurde weiter gereinigt durch Herstellung und darauffolgende Zersetzung ihres Lithiumsalzes[7]. Die Säure wurde schließlich in Form farbloser glänzender Kristalle erhalten, Schmp. 29 bis 30° C und JZ 89.5. Die reine Säure ergab bei der Elaidinierung Δ-6-trans-Octadecen(Petroselaidin)säure, Schmp. 52 bis 53° C. Bei Oxydation mit Permanganat wurde Threo-6,7-dihydroxyoctadecansäure, Schmp. 115 bis 116° C erhalten. Die Zusammensetzung der Fettsäuren wurde nach der Esterfraktionierungs-Methode wie folgt bestimmt: Harzsäuren 3% und Fettsäuren (als Differenz) 97%, und zwar 6.18% Palmitinsäure 46.06% Petroselinsäure, 30.96% Ölsäure und 13.8% Linolsäure.

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N° 152. — Étude chimique des lipides de la graine d'Albizzia odoratissima, Benth.,

par M. O. FAROOQ et Saleem SIDDIQUI.

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L'huile fixe des graines d'Albizzia odoratissima, Benth. a été analysée par la méthode de fractionnement des esters : la composition du mélange des acides gras est la suivante : acide palmitique : 14,33 %, stéarique : 6,88 %, arachidique : 0,81 %, oléique : 26,56 % et linoléique : 51,42 %.

L'Albizzia odoratissiam, connue sous le nom de « Kala siris » (1) en Hindi, appartient à la sous-famille des Mimosées de la famille des Légumineuses. Les parties utilisées dans cette plante sont l'écorce et les feuilles qui sont considérées comme efficaces contre la lèpre, les ulcères chroniques et la toux (2). Comme il semble qu'aucun travail n'ait été fait sur l'huile de sa graine, il nous apparut intéressant de l'étudier et de la comparer avec celle de la graine du seul membre du genre Albizzia étudié jusqu'ici, l'Albizzia lebbek. Les résultats comparatifs des graisses des deux membres du genre Albizzia sont donnés dans le tableau I.

Ces résultats montrent que l'huile de la graine d'Albizzia odoratissima, Benth. diffère par sa composition de celle d'Albizzia lebbek. Elle contient plus d'acides non saturés que celle d'Albizzia lebbek, compte tenu de la proportion beaucoup plus grande d'acide linoléique, qui représente la moitié de la quantité des acides totaux. En ce qui concerne les acides supérieurs (C_{20} — C_{24}), il est intéressant de noter que l'huile d'Albizzia odoratissima contient seulement des traces d'acide arachidique, qui forme la majeure partie des acides saturés dans le cas de l'Albizzia lebbek (5, 6). L'acide myristique est absent, ce qui est conforme à nos recherches dans le cas de deux autres membres (5, 6) de cette sous-famille. La présence d'acide palmitique comme composant majeur de cette huile est en accord avec la généralisation de Grindley (*loc. cit.*) sur les huiles des graines de cette sous-famille. L'identité de ces acides fut établie dans les fractions spécifiques des esters méthyliques des acides solides.

Les acides liquides obtenus furent les acides oléique et linoléique. Le rapport de l'acide oléique à l'acide linoléique est de 1 : 2 et non de 2 : 1 à 3 : 4 comme l'a noté Grindley

dans le cas des huiles de graines de cette sous-famille au Soudan (4). L'identité de ces acides a été confirmée par la formation d'acide tétrabromostéarique et des acides di- et tétra-hydroxystéariques.

TABLEAU I.

Acides	Albizzia lebbek			Albizzia odoratissima
	(3) KAFUKU et HATA 1934 %	(4) GRINDLEY 1945 %	(5) FAROOQ et VARSHNEY %	FAROOQ et SIDDIQUI
Saturés	29,0	29,0	27,78	22,02
Palmitique	petites quantités	la plus grande partie	7,26	14,33
Stéarique	—	—	9,63	6,88
Arachidique	la plus grande partie	—	10,89	0,81
Myristique	petites quantités	—	—	—
C_{20}-C_{24}	—	3,1	—	—
Non saturés	71,0	71,0	72,22	77,98
Oléique	présent	43,0	39,28	26,56
Linoléique	présent	28,0	32,94	51,42

PARTIE EXPÉRIMENTALE.

Un examen préliminaire de l'huile obtenue à partie des graines séchées et pulvérisées, par extraction avec l'éther de pétrole (Eb = 40-60°), donna les résultats suivants :

TABLEAU II.

Teneur en graisse	3,4 %
D. à 32°	0,9116
Indice de réfraction à 32°	1,47[illegible]
Indice de saponification	174,9
Indice d'iode	114,5
Insaponifiable	5,7 %

L'huile extraite fut saponifiée avec de la potasse alcoolique et la partie insaponifiable enlevée à l'éther. Le mélange des acides gras fut isolé (87,5 %) et les acides séparés

TABLEAU III.

	Indice d'iode	Indice de saponificatien	P. M. moyen calculé
Acides totaux	129,2	197,8	283,6
Acides liquides	143,4	200,15	280,3
Acides solides	4,2	200,65	279,5

TABLEAU IV

Esters méthyliques des acides liquides.

Fractions	Poids en g	P. E./3 mm	Indice d'iode	Indice de saponification	Composition calculée en g			
					Palmitate	Oléate	Linoléate	Insaponifiable
L_1	5,83	jusqu'à 170°	133,3	282,2	0,58	2,34	2,91	—
L_2	5,56	170-172°	144,6	285,6	0,13	1,71	3,72	—
L_3	7,23	172-173°	148,1	290,3	—	1,99	5,24	—
L_4	4,53	173-175°	142,9	293,9	—	1,52	3,01	—
L_5	5,98	Résidu	105,8	279,0	—	1,97	3,90	0,11
Total	29,13				0,71	9,53	18,78	0,11
		Pour cent en esters			2,44	32,72	64,47	0,37
		Pour cent en acides			2,42	32,73	64,48	0,37

TABLEAU V

Esters méthyliques des acides solides.

Fractions	Poids en g	P. E./3 mm	Indice d'iode	Indice de saponification corrigé	Composition calculée en g			
					Palmitate	Stéarate	Arachidate	Non saturés
S_1	4,55	jusqu'à 160°	1,64	271,9	4,13	0,33	—	0,09
S_2	3,87	160-170°	0,97	273,6	3,30	0,53	—	0,04
S_3	7,40	170-175°	1,0	282,4	3,90	3,50	—	0,08
S_4	2,86	Résidu	6,53	305,3	—	1,90	0,74	0,22
Total	18,76				11,33	6,26	0,74	0,43
		Pour cent en esters			60,40	33,36	3,94	2,30
		Pour cent en acides			60,70	33,46	3,97	2,30

en leurs constituants liquides et solides par la méthode de Twitchell au plomb et à l'alcool; ils se composaient de 20,5 % d'acides solides et de 79,5 % d'acides liquides. La quantité d'acides saturés déterminée par la méthode de Bertram modifié correspondait à 21 % des acides totaux. Les trois groupes d'acides gras avaient les caractéristiques ci-contre Tableau III :

Les acides solides et liquides furent convertis séparément en leurs esters méthyliques, et systématiquement fractionnés sous vide. Le calcul de la composition de chaque fraction d'ester a été fait, selon Baughman et Jamieson (8), d'après les chiffres des indices d'iode et de saponification en même temps que d'après les résultats de l'examen qualitatif des fractions respectives. Les résultats du fractionnement des esters sont indiqués ci-contre Tableau IV et V :

Les acides palmitique, stéarique, arachidique, oléique et linoléique furent identifiés dans les fractions d'ester comme nous l'indiquons ci-dessous :

Identification des acides gras.

S_1-S_3	Acide palmitique,	= P.F. 57-59°.
	Acide stéarique,	= P.F. 68-70°.
S_4	Acide stéarique,	= P.F. 68-70°.
	Acide arachidique,	= P.F. 73-75°.
L_1-L_2	Acide palmitique,	= P.F. 59-61°.
	Acide dihydroxystéarique,	= P.F. 130-132°.
	Acide tétrahydroxystéarique,	= P.F. 170-172°.

La bromuration des acides liquides dérivés des esters (L_3-L_5) donna un tétrabromure cristallisé, F = 113-114°. On ne put isoler aucun hexabromure insoluble dans l'éther, ce qui confirme l'absence d'acide linolénique dans les acides liquides. Tous les efforts pour isoler l'acide myristique dans les fractions de l'ester méthylique des acides solides furent infructueux.

La composition des acides gras totaux, déterminée par la méthode de fractionnement des esters, était la suivante : acide palmitique, 14,33 %, stéarique 6,88 %, arachidique 0,81 %, oléique 26,56 % et linoléique 51,42 %.

Les auteurs désirent exprimer leur reconnaissance au Gouvernement de l'Inde, au Ministre de l'Education, pour l'attribution d'une bourse de recherche à l'un d'eux et aussi au Docteur M. A. Aziz et à M. S. M. Osman, pour l'intérêt qu'ils ont porté à ce travail.

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ÉTUDE CHIMIQUE DE L'HUILE DE LA GRAINE D'*ALBIZZIA PROCERA* BENTH.

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Albizzia procera Benth, connue sous le nom de « Safid Siris » en Hindi appartient à la sous-famille des Mimosées, de la famille des Légumineuses. Comme il semble qu'aucun travail n'ait été fait sur l'huile de sa graine et comme de grandes quantités d'huile avaient été recueillies au cours de notre étude sur la saponine de cette plante [1, 2, 3] pendant laquelle des quantités considérables de graines avaient dû être dégraissées, il nous apparut désirable et intéressant d'entreprendre l'étude de l'huile et de la comparer avec celle des graines d'autres espèces d'*Albizzia*.

Nous donnons ci-après un tableau comparatif de la composition des acides totaux de cette huile et celle des autres espèces.

Le présent travail montre que l'huile de la graine d'*Albizzia procera* Benth. diffère par sa composition de celles d'autres espèces d'*Albizzia*. Elle contient comparativement plus d'acides saturés que celle de toutes les autres espèces d'*Albizzia*. Elle contient des proportions beaucoup plus grandes d'acide oléique qui représente la moitié de la quantité des acides totaux (50,89 p. 100). Les proportions d'acide stéarique et d'acide arachidique sont aussi plus élevées que celles des autres espèces. L'absence de l'acide myristique, comme dans les autres espèces d'*Albizzia* [6, 7] est notable. Sa présence est signalée seulement par Chandra et ses coll. [8] qui ont étudié des graines provenant du sud de l'Inde où le climat est différent.

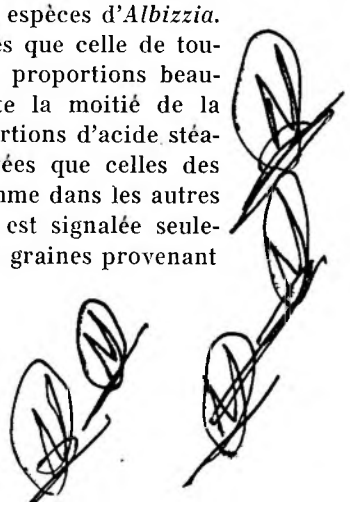

TABLEAU I.

Acides	*Albizzia lebbek*			*Albizzia odoratissima* Farooq et Siddiqui 1954 [7] p. 100	*Albizzia amara* Chandra et al. 1956 [8] p. 100	*Albizzia procera* Cette étude 1958 p. 100
	Kafuku et Hata 1934 [4] p. 100	Grindley 1945 [5] p. 100	Farooq et Varshney 1954 [6] p. 100			
Saturés	29,0	29,0	27,78	22,02	17,57	33,70
Myristique	Petites quantités	—	—	—	1,62	—
Palmitique	Petites quantités	la plus grande partie	7,26	14,33	8,04	7,23
Stéarique	—	—	9,63	6,88	4,55	14,26
Arachidique	la plus grande partie	—	10,89	0,81	2,30	12,21
$C_{20} - C_{24}$	—	3,1	—	—	Behinique 0,61 Lignoserique 0,45	—
Non-saturés	71,0	71,0	72,22	77,98	82,43	66,30
Oléique	présent	43,0	39,28	26,56	33,18	50,89
Linoléique	présent	28,0	32,94	51,41	49,25	15,41

Partie expérimentale.

Les graines sèches finement pulvérisées, provenant de l'Etat de Madhya Pradash (Inde), récoltées il y a trois ans donnèrent par extraction avec de l'éther de pétrole (40-60°) une huile jaune-verdâtre (6 p. 100), (cf. *Albizzia lebbek* [6], 3,5 p. 100 et *Albizzia odoratissima* [7], 3,4 p. 100) ayant une odeur typique ressemblant à celle d'*Albizzia lebbek* Benth [6], avec les caractères suivants :

TABLEAU II.

Teneur en graisse.....	6,0 p. 100
d a 25°.....	0,9423
Indice de réfraction à 25°.....	1,4512
Indice de saponification.....	185,4
Indice d'iode.....	90,1
Insaponifiable.....	7,1 p. 100

L'huile (100 g) fut saponifiée avec une solution alcoolique de potasse. Après avoir chassé l'alcool, le savon a été dissous dans l'eau et la solution aqueuse fut soigneusement extraite à l'éther. Les acides gras libres du savon à la manière habituelle, furent alors séparés en acides gras solides et liquides en employant la méthode à l'alcool et au plomb de Twitchell, modifiée par Hilditch [9].

Les trois groupes d'acides gras ont les constantes suivantes :

TABLEAU III.

Acides	p. 100	Indice d'iode	Indice de saponification
Acides totaux.....	76,0	95,2	197,02
Acides liquides.....	35,8	9,5	187,2
Acides solides.....	64,2	99,5	189,9

Les acides gras liquides et solides ont été convertis séparément en esters méthyliques avec de l'alcool méthylique, les esters soumis à la distillation fractionnée sous pression réduite (2 mm). La composition de chaque fraction d'esters a été calculée d'après les valeurs de l'indice d'iode et de l'indice de saponification selon la méthode de Baughman et Jamieson [10]. Les résultats du fractionnement des esters sont indiqués ci-contre (Tableaux IV et V).

TABLEAU IV.

ESTERS MÉTHYLIQUES DES ACIDES LIQUIDES.

Fractions	Poids en g	P. Eb./2 mm	Indice d'iode	Indice de saponification	Composition calculée en g		
					oléate	linoléate	saturés : palmitate
L_1.....	11,25	Jusqu'à 176°	103,4	270,1	8,11	2,05	1,09
L_2.....	12,68	176-80°	114,4	282,2	8,52	4,16	—
L_3.....	15,70	180-82°	105,1	283,6	12,22	3,48	—
L_4.....	12,41	Résidue	87,4	290,6	9,66	2,75	—
Total...	52,04				38,51	12,44	1,09
		p. 100 en esters.....			74,00	23,91	2,09
		p. 100 en acides			73,90	24,01	2,09

TABLEAU V.

ESTERS MÉTHYLIQUES DES ACIDES SOLIDES.

Fractions	Poids en g	P. Eb./2 mm	Indice d'iode	Indice de saponification	Composition calculée en g			
					palmitate	stéarate	arachidate	non saturés
S_1....	4,32	Jusqu'à 168°	11,9	275,8	2,90	0,83	—	0,59
S_2....	4,96	168-70°	8,5	290,7	0,69	3,78	—	0,49
S_3....	7,57	170-74°	4,7	313,2	—	3,12	4,04	0,41
S_4....	4,82	Résidu	10,7	319,6	—	0,90	3,32	0,60
Total.	21,67				3,59	8,63	7,36	2,09
		p. 100 en esters.....			16,56	39,87	33,93	9,64
		p. 100 en acides.....			16,42	39,85	34,10	9,63

Identification des acides gras.

Acides saturés : Une portion de chaque fraction des esters méthyliques des acides solides a été saponifiée et les acides gras libérés de la manière habituelle. Les acides gras libres ont été cristallisés par fractionnement et ont donné les acides purs identifiés par leurs points de fusion et leurs points de fusion mélangés avec des échantillons authentiques. Dans quelques cas, les acides sont purifiés par précipitation fractionnée des acides sous forme de sel de magnésium, suivie de la décomposition de ces sels.

TABLEAU VI.

IDENTIFICATION DES ACIDES GRAS.

Fractions		P. F.
S_1 - S_2	Acide palmitique	57-59°
	Acide stéarique	69-70°
S_3	Acide stéarique	69-70°
	Acide arachidique	73-74°
L_1	Acide palmitique	59-60°
L_1 - L_4	Acide dihydroxystéarique	130-31°
	Acide tetrahydroxystéarique	170-71°
L_1 - L_3	Acide tetrabromostéarique	114-15°

Acides non-saturés : Les deux acides non-saturés présents dans les acides liquides furent identifiés en oxydant les acides libres de chaque fraction des esters après saponification avec une solution de permanganate de potassium alcaline refroidie à 0°.

Les acides saturés ainsi obtenus (acide dihydroxy-stéarique et acide tétrahydroxy-stéarique) furent identifiés dans toutes les fractions acides liquides (L_1 a L_4) par leurs points de fusion et leurs points de fusion mélangés avec des échantillons authentiques. Tous les essais en vue d'isoler l'acide hexahydroxy-stéarique ayant échoué il faut en conclure à l'absence de l'acide linolénique. Une preuve supplémentaire de la présence de l'acide linolénique fut obtenue par l'isolement d'acide tétra-bromo-stéarique sans dépression de son point de fusion par mélange avec un échantillon authentique. L'absence d'acide linolénique fut établie et confirmée par la non-formation de dérivé hexabromé dans toutes les fractions de l'ester méthylique de l'acide liquide.

La composition des acides gras totaux déterminée par la méthode de fractionnement des esters méthyliques était la suivante :

TABLEAU VII.

COMPOSITION CALCULÉE DU MÉLANGE DES ACIDES GRAS.

Acides	Solides p. 100	Liquides p. 100	Total p. 100
Saturés			
1. Palmitique.....	5,88	1.35	7.23
2. Stéarique.....	14.26	—	14.26
3. Arachidique.....	12.21	—	12.21
Non saturés			
4. Oléique.....	3.45	47.44	50,89
5. Linoléique.....	—	15.41	15,41

RÉSUMÉ.

L'huile fixe des graines d'*Albizzia procera* Benth a été analysée et sa composition en acides gras déterminée par la méthode de fractionnement des esters. La composition en acides gras des acides totaux de l'huile serait : acide palmitique 7,23 p. 100 ; acide stéarique, 14,26 p. 100 ; acide arachidique, 12,21 p. 100 ; acide oléique, 50,89 p. 100 ; acide linoléique, 15,41 p. 100.

SUMMARY.

Fixed oil from the seeds of *Albizzia procera* Benth has been analysed and its fatty acid composition determined by the method of ester fractionation. The fatty acid composition of the total acids of the oil appears to be : palmitic acid 7,23 p. 100 : stearic acid 14,26 p. 100 ; arachidic acid 12,21 p. 100 ; oleic acid 50,89 p. 100 ; linoleic acid 15,41 p. 100.

ZUSAMMENFASSUNG.

Das beständige Oel der Samen von *Albizzia procera* Benth wurde untersucht und seine Zusammensetzung an Fettsäuren wurde durch die Esterfraktionierungsmethode bestimmt. Diese Zusammensetzung wäre, im Verhältnis zu den totalen Fettsäuren des Oels : Palmitinsäure 7,23 p. 100 ; Stearinsäure 14,26 p. 100 ; Arachinsäure 12,21 p. 100 ; Oelsäure 50,89 p. 100 ; Linoleinsäure 15,41 p. 100.

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IMPRIMERIE MAURICE DECLUME, LONS-LE-SAUNIER.

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Chemical Investigation of the Seed-Oil of Leucaena Glauca, Benth.

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LEUCAENA GLAUCA, a tree indigenous to India, belongs to the sub-family Mimosacae of the N. O. Leguminosae. The seeds and leaves are used as a valuable food for cattle (1). A review of the literature indicates that the seed oil of the Formosan variety has been examined by Kinzo Kafuku and his collaborators (2), who reported that the oil contains 29% saturated acids (myristic, palmitic, stearic, behenic), and 71% unsaturated acids (equal amounts of oleic and linoleic acids). As their results do not give a clear account of the percentage of individual acids, the present authors considered it of interest to subject the oil from the Indian variety to a more systematic chemical examination by applying the ester-fractionation method.

The presence of oleic and linoleic acids was established by the bromination and oxidation of the fatty acids derived from the lead-salts soluble in alcohol, but no linolenic could be detected, thus lending support to the view put forward by Grindley (3) that the latter acid is absent in any of the oils belonging to this sub-family so far investigated. Palmitic, stearic, behenic, and lignoceric acids were identified in specific fractions of the hydrolyzed "solid" esters. Attempts to isolate any lower acid other than palmitic failed to disclose the presence of myristic acid, but, on the other hand, lignoceric acid (0.67%) has been found to occur in this oil, not mentioned earlier. Quantitative estimation of the composition of the mixed fatty acids of this oil shows that it differs from that of Formosan variety. Further, it is interesting to note that the major component acids (oleic and linoleic) of this oil are nearly in the proportion of 1:2 whereas this ratio in the case of Mimosacae seed-oils of Sudan varies from 2:1 to 3:4, according to the species (3).

Experimental

The dried and finely powdered seeds on extraction with petroleum ether (b.p. 40-60°C.) gave a dark green oil, bearing the following characteristics:

Fat content	8.8%
Sp. Gr. at 28°C	0.91648
Ref. Index at 28°C	1.4674
Sap. value	184.95
I.V. (Hanus)	110.11
Acidity (as % oleic)	2.97
Unsaponifiable	4.7%

The oil on saponification and subsequent hydrolysis, after removal of unsaponifiable matter, yielded 91.5% of free fatty acids. The fatty acids were then resolved into their solid and liquid components by Twitchell's lead-salt-alcohol process and found to be composed of 20.3% solid and 79.7% liquid acids. An estimation of the saturated acids by modified Bertram's method (4) gave 20.8% of saturated acids.

The three groups of fatty acids have the following constants:

	I.V.	S.V.	Calc. Mean Mol. Wt.
Total acids	111.5	200.5	279.8
Liquid fatty acids	135.3	199.9	280.7
Solid fatty acids	6.2	206.2	272.6

TABLE I

Methyl Esters of Liquid Acids

Fr.	Wt./g.	B.P./3 mm.	I.V.	S.E.	Calculated composition Wt./g.			
					Palmitate	Oleate	Linoleate	Unsap.
L_1	10.30	up to 158°C.	124.5	285.3	1.57	2.58	6.15	.....
L_2	13.73	158-62°	142.15	291.9	0.51	3.91	9.31	.....
L_3	11.71	162-64°	146.65	293.2	0.08	3.44	8.19	.....
L_4	12.20	164-68°	146.8	293.8	.....	3.61	8.59	.....
L_5	10.67	168° falling	139.3	290.9	.....	3.16	7.51	.....
L_6	11.95	Residue [a]	77.0	333.1	.....	3.39	8.08	0.48
Total	70.56				2.16	20.09	47.83	0.48
			% as esters		3.06	28.48	67.78	0.68
			% as acids		3.05	28.50	67.77	0.68

TABLE II

Methyl Esters of Solid Acids

Fr.	Wt./g.	B.P./4 mm.	I.V.	S.E. (corrected)	Calculated composition Wt./g.				
					Saturated				Unsaturated Oleate
					C_{16}	C_{18}	C_{20}	C_{24}	
S_1	5.87	up to 163°C.	1.68	271.2	5.50	0.27	.....	.....	0.10
S_2	6.83	163-65°	1.61	274.3	5.58	1.12	.....	.....	0.13
S_3	7.65	165-67°	2.37	277.3	5.36	2.08	.....	.....	0.21
S_4	4.92	167-72°	4.00	289.3	1.30	3.39	.....	.....	0.23
S_5	2.32	172-83°	4.71	308.4	.....	1.72	0.47	.....	0.13
S_6	7.43	Residue	6.40	358.4	.....	.....	5.73	1.15	0.55
Total	35.02				17.74	8.58	6.2	1.15	1.35
			% as esters		50.66	24.50	17.7	3.28	3.86
			% as acids		50.43	24.51	17.85	3.32	3.89

[a] S.E. of L_6 after removal of unsaponifiable = 305.3. The high S.E. of L_6 even after correction for unsaponifiable indicates the possibility of the presence of small amounts of C_{20} unsaturated acids. We have preferred however to leave this open and include all in oleic and linoleic on the basis of the I.V. of the previous fraction (L_5).

The liquid and solid fatty acids were separately converted into methyl esters and systematically fractionated under vacuum. The percentages of the individual saturated acids in each ester fraction have been calculated according to the method of Baughman and Jamieson (5). The amounts of palmitic and C_{18} mono- and di-ethenoid acids and unsaponifiable in liquid esters are estimated on the basis of iodine values and saponification equivalents in conjunction with qualitative examination of each ester fraction. The results of the ester-fractionation are tabulated below.

Identification of Fatty Acids

Unsaturated acids. The oleic and linoleic acids were identified in the "liquid" ester fractions (L_1-L_5) in the form of their oxidation products (9:10 dihydroxy-stearic acid, m.p. 130°C.; 9:10:12:13 tetrahydroxy-stearic acid, m.p. 174°C.) obtained by the permanganate oxidation of the regenerated acids. Traces of palmitic acid (m.p. 59-61°) were isolated in the lowest boiling fractions (L_1-L_3) of liquid acid esters from light petroleum ether extracts of the oxidized product, followed by crystallization from aqueous alcohol. Further evidence of the presence of linoleic acid was obtained by the isolation of a tetrabromide m.p. 113-14° (which showed no depression on admixture with an authentic sample). No ether-insoluble hexabromide could be isolated, thus confirming the absence of linolenic acid in the liquid acids.

Saturated acids. The acids from each ester fraction were isolated and identified by their melting and mixed melting points.

Fractions

S_1-S_4: Palmitic acid, m.p. 59-61°; stearic acid, m.p. 69-71°.

S_5: Stearic acid, m.p. 68-70°; behenic acid, m.p. 78-80°.

S_6: Behenic acid, m.p. 78-80°, mean. mol. wt., 344.5 lignoceric acid, m.p. 78-80°, mean. mol. wt., 366.2.

The S.E. of the residue (S_6), which is in between that of methyl-behenate and methyl-lignocerate, clearly indicates their presence in this fraction.

TABLE III

Calculated Composition of Total Fatty Acids

	Solid	Liquid	Total	Excluding unsaponifiable
	%	%	%	%
	20.3	79.7	100.0	
Saturated acids				
Palmitic	10.24	2.43	12.67	12.74
Stearic	4.98	.....	4.98	5.01
Behenic	3.62	.....	3.62	3.64
Lignoceric	0.67	.....	0.67	0.67
Unsaturated acids				
Oleic	0.79	22.71	23.50	23.63
Linoleic	.....	54.01	54.01	54.31
Unsaponifiable	.....	0.55	0.55	.....

Examination of the Unsaponifiable Matter

The unsaponifiable matter obtained, prior to the liberation of the mixed fatty acids, when crystallized from absolute alcohol gave white crystalline needles m.p. 139-40°C. This appears to be sitosterol.

Summary

The fixed oil from the seeds of *Leucaena glauca*, Benth. (N. O. Leguminosae) has been studied for its component acids. The fatty acid composition, as determined by the ester-fractionation analysis, was found to be palmitic (12.74%), stearic (5.01%), behenic (3.64%), lignoceric (0.67%), oleic (23.63%), and linoleic (54.31%). The latter unsaturated acids are the major components.

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Chemische Untersuchung des Samenfettes von Haloptela integrifolia

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Das fette Öl der Samen von Haloptela integrifolia wurde nach der Esterfraktionierungsmethode analysiert, wobei die folgende Zusammensetzung der gemischten Fettsäuren gefunden wurde: 37.64 % Palmitinsäure, 10.04 % Stearinsäure, 2.03 % Arachidonsäure, 46.66 % Ölsäure und 3.63 % Linolsäure.

Examen chimique des matières grasses contenues dans la graine de l'Haloptela integrifolia

L'huile grasse des graines de l'Haloptela integrifolia, a été analysée par la méthode de fractionnement des esters, au moyen de laquelle, on a trouvé la composition suivante pour le mélange des acides gras: 37.64 % d'acide palmitique; 10.04 % d'acide stéarique; 2.03 % d'acide arachidique; 46.66 % d'acide oléique et 3.63 % d'acide linoléique.

Análisis químico de la grasa de la semilla de la Haloptela integrifolia

Se analizó el eceite de las semillas por el método del fraccionamiento de los ésteres, y se encontró que tiene la siguiente composición de ácidos grasos mixtos: palmítico 37.64 %, esteárico 10.04 %, araquídico 2.03 %, oléico 46.66 % y linoléico 3.63 %.

Chemical Investigation of the Seed-fat of Haloptela integrifolia

The fixed oil from the seeds of Haloptela integrifolia has been analysed by the ester-fractionation method and found to have the following composition of the mixed fatty acids; palmitic 37.64 %, stearic 10.04 %, arachidic 2.03 %, oleic 46.66 % and linoleic acid 3.63 %.

Haloptela integrifolia, gemeinhin als „Papri" bekannt und zur Familie der Urticaceen gehörend, ist ein großer in den niederen Gebieten des Himalaya vorkommender Baum. In der Literatur finden sich nur einige Angaben von *S. N. Chatterji* und *R. K. Gobhil*[1], die einzelne physikalisch-chemische Konstanten des Fettes bestimmten, es aber sonst nicht weiter untersuchten. Die Tatsache, daß die Samen eßbar sind und verhältnismäßig viel (50.5 %) Fett enthalten, welches wie Butter aussieht, erweckte unsere Aufmerksamkeit.

Es erschien deshalb wünschenswert, das Fett einer systematischen chemischen Untersuchung zu unterwerfen und seine Fettsäure-Zusammensetzung zu bestimmen.

Experimentelles

Die gesammelten, fein gepulverten und getrockneten Samen wurden mit Petroläther (Sdp. 40 bis 60° C) extrahiert. Das auf diese Weise erhaltene Fett hatte die folgenden Konstanten:

Fettgehalt der Samen	50.5 %
d 21°	0.9011
n^{21}_D	1.4690
VZ	197.9
JZ *(Wijs)*	46.2
Unverseifbares	2.9 %

Das extrahierte Fett wurde mit alkoholischer Kalilauge verseift und das Unverseifbare mit Äther ausgeschüttelt. Das Fettsäure-Gemisch wurde dann abgetrennt (86.00 %). Mit Hilfe der Bleisalz-Alkohol-Methode von *Twitchell* wurden die Fettsäuren in ihre festen und flüssigen Komponenten zerlegt, wobei 51.80 % feste und 48.20 % flüssige Säuren erhalten wurden. Die drei Gruppen von Fettsäuren hatten die folgenden Kennzahlen:

	JZ *(Wijs)*	Verseifungs-äquivalent
Gesamtfettsäuren	51.9	273.2
Fe		
F'		

ren geht hervor, daß diese Gruppe in der Hauptsache aus Ölsäure besteht. Die Jodzahlen der Fraktionen L_2 bis L_4 sind höher als die des reinen Methyloleats (85). Diese Fraktionen enthalten also anscheinend Spuren von Linolsäure, deren Nachweis wegen ihrer geringen Menge schwierig ist. In Anbetracht der Tatsache, daß Öl- und Linolsäure bei den meisten Samenfetten zusammen vorkommen, haben die Verfasser ihr Verhältnis aus den Jodzahlen der betreffenden Fraktionen berechnet, indem sie sie als binäres Gemisch auffaßten. Die Resultate der Esterfraktionierung sind in den folgenden Tabellen wiedergegeben:

Tabelle 1

Methylester der festen Säuren

Fr.	Gew. in g	Sdp. 3 mm	JZ	Verseifungs-äquivalent	Berechn. Zusammensetzung Gew. in g: Palmitat	Stearat	Arachinat	Ungesättigt
S_1	6.03	Bis zu 152°	3.7	270.8	5.77	—	—	0.26
S_2	5.83	152—53°	3.7	274.0	4.80	0.78	—	0.28
S_3	4.78	153—54°	4.2	275.5	3.65	0.90	—	0.23
S_4	5.46	154—56°	6.2	277.9	3.61	1.46	—	0.39
S_5	3.50	Rückstand	16.6	307.8	—	1.82	1.00	0.68
Insgesamt 25.6					17.83	4.92	1.00	1.81
				% Ester	69.65	19.37	3.91	7.07
				% Säuren	69.64	19.38	3.91	7.07

Tabelle 2

Methylester der flüssigen Säuren

Berechn. Zusammensetzung Gew. in g

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Identifizierung der Fettsäuren

Zum Zwecke der Identifizierung wurden die verschiedenen Esterfraktionen hydrolysiert. Die freigemachten Säuren wurden der fraktionierten Kristallisation unterworfen. Palmitin-, Stearin- und Arachinsäure wurden in den festen Fraktionen identifiziert.

Fraktionen:

S_1	Palmitinsäure, Schmp. 58—60°
S_2—S_4	Palmitinsäure, Schmp. 57—59°
	Stearinsäure, Schmp. 68—70°
S_5	Stearinsäure, Schmp. 68—70°
	Arachinsäure, Schmp. 73—75°

Die Esterfraktionen der flüssigen Fettsäuren L_1—L_4 wurden in ähnlicher Weise hydrolysiert und die erhaltenen Seifen mit eiskalter, verdünnter alkalischer Permanganat-Lösung oxydiert. Das freigemachte Gemisch von Hydroxystearinsäuren wurde mit Petroläther erhitzt, um gesättigte Fettsäuren zu entfernen; nur Palmitinsäure, Schmp. 59—60°, wurde in Fraktion L_1 gefunden; die letztere wurde durch Kristallisation aus Alkohol gereinigt. Die rohen Hydroxystearinsäuren wurden mit Wasser ausgekocht, um gebildete Sativinsäure zu entfernen, und die Hydroxysäure wurde danach aus Alkohol umkristallisiert. Nur Ölsäure konnte in der Form der entsprechenden 9,10-Dihydroxystearinsäure, Schmp. 130—133° C, festgestellt werden.

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